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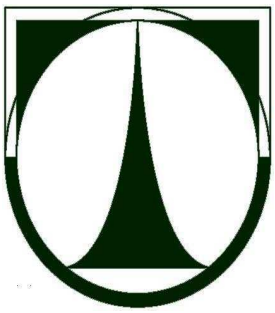
Faculty of Textile Engineering



DIPLOMA THESIS

2010 **Khensani Nkuna**

Technical University of Liberec
Faculty of Textile Engineering
Department of Textile Chemistry

Special Textile Finishing – Microencapsulation

Khensani Nkuna

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The number of text pages : 68
The number of pictures : 48
The number of tables : 13
The number of graphs : 13
The number of appendices : 8

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Acknowledgements

I would like to thank my supervisor, Ing. Bc. Jana Šašková, MSc for her assistance in gathering information and advices. I'm also thankful to Assoc. Prof. Eng. Jakub Wiener, Ph.D. for his professional experience, advices and his knowledge of textile.

I am very thankful to Marie Štěpánková, MSc for her assistance in the laboratory; I would have not made so much progress without her help. I am thankful to the staff at the Department of chemistry, laboratory assistance for their help and assistance in term of chemicals and equipments.

I am also thankful to Ing Vladimir Kovacic for his professional experience in scanning of images and to Ing Jana Grabmullerova for her assistance in the department of materials. I am thankful to Ing Jirí Chvojka his assistance and to the PhD students and staff at the department of nonwoven.

I would like to give special thanks to my mother Maggy Nkuna for all her support during my study and completion of my Thesis. All the hard work I have put on this project it is all because of her encouragement and support towards my studies. I am thankful to my family and friends for their support. I am also thankful to my fiancé Siviwe Mfuywa for his support and guidance.

I would like to thank the Technical University of Liberec for giving me this opportunity to study and finish my Diploma Thesis. I have learned a lot through this experience.

Annotation

Textile finishing has always been an important component of textile processing. In recent years the use of high performance textile has developed, special finishes on textile has been developed due to the variability of fashion influences and higher quality requirements. This special finish was made to provide final product which gives special properties to the fabric, and for the fabric to be suited for specific uses.

Several special finishes have been developed in addition to the normal finishing process, anti-static finishes, anti-soiling finishes, and flame-retardant impregnation, water-repellent finishes, non-crease finishes, shrink proof finishes, permanent finishing and water-proof finishing.

Microencapsulation is one of the special finishes applied on a textile. Microencapsulation technologies involve an encapsulated of a compound inside a tiny sphere known as microcapsule, in which various active materials such as drugs, vitamins and flavors are effectively encapsulated with a formation of microcapsules. These microcapsules release their contents at appropriate time by using different release mechanisms.

The aim of this thesis was to produce micro-particles of sodium chloride using the physical process of microencapsulation. Spray drying process was used for formation of powder of sodium chloride containing micro-particles; the particles were measured and analyzed. The powdered form was applied on a fiber samples consisting of bicomponent fibers for observation of any changes in the fiber properties.
The second objective was to produce microcapsules of phase change material using spray drying process. Paraffin wax was used as a phase change material. Microcapsules were measurements and analyzed according to the distribution of the microcapsules.

List of abbreviations

1. Microencapsulation-MIC
2. Micrometers-µm
3. Millimeters-ml
4. Liters-l/L
5. Grams-g
6. Meters-m
7. Minutes-min
8. Kilogram-kg
9. KJ-Kilojoules
10. Joules-J
11. Kelvin-K
12. Degrees Celsius-^{O}C
13. Phase change material-PCM
14. Latent heat storage-LHS
15. Sodium chloride-NaCl
16. Sodium sulphate-Na_2SO_4
17. Calcium chloride-$CaCl_2$
18. Polyethylene terephthalate-PET
19. Diethylene glycol-DEG
20. Copolyester/polyester-CO/PES
21. Temperature-T
22. Glass transition temperature-Tg
23. Crystallization temperature-Tc
24. Melting temperature-Tm
25. Weight by weight-w/w
26. Scanning electron microscope-SEM
27. Differential scanning calorimetry-DSC

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1. Introduction

Microencapsulation is a process in which tiny particles or droplets are surrounded by a coating to give small capsules. It may also be defined as the process of surrounding or enclosing one substance with another substance on a very small scale, which yields to capsules ranging from less than one micron to several hundred microns in size [1].

Microencapsulation may be achieved by various techniques, such as substance that are microencapsulated with the intension that the core material is enclosed within the capsule walls for a specific period of time. Another method is that the core materials may be encapsulated and released either evenly through the capsule walls, which is known as controlled release or when external conditions generates and causes the capsule walls to melt or dissolve [2].

Microencapsulation can provide a physical barrier between the core compound and the other components of the product. The material inside the microcapsule is known as the core (internal phase or fill), whereas the wall is often called a shell or coating [3]. Thus, the shell either permanently or temporarily protects the core. Practically, the core may be a crystalline material, an adsorbent particle (emulsion, suspension of solids, or a suspension of smaller microcapsules). The microcapsule may even have multiple walls. Microcapsules have a size range of about 50 nm to 2000 µm or larger [1].

Microencapsulation is defined as a process in which very thin coatings of inert materials are deposited around micro-sized particles of solids or droplets of liquids or gasses. The inertness relates to the reactivity of the shell with the core. The shell can be made from natural or synthetic polymers applied as solutions, latexes or fat derivatives and proteins. Shell materials that are widely used are gelatin, starches, cellulose derivatives, polyvinyl alcohols, acrylates, fats and waxes [8]. Three states of matter (solids, liquids and gases) can be microencapsulated so as the core material is microencapsulated in the form of a solution, emulsion or dispersion [1]. Compatibility of core material with the polymer shell is vital for efficient microencapsulation. The core is also strongly dependent on the experimental conditions such as pH, solvent, temperature and other factors.

2. Theoretical part

2.1 Methods of producing microcapsules

Several microencapsulation techniques have been developed, including the chemical method which consists of suspension, dispersion and emulsion (polycondensation and polymerization). Physical method are subdivided into two techniques known as physico-chemical (coacervation, sol-gel encapsulation), and physico-mechanical techniques (spray encapsulation).
The selection of these techniques and shell material depends on the final application of the product, considering physical and chemical stability, concentration, desired particle size, release mechanism, and manufacturing costs.

Table 1: Types of microencapsulation techniques

Chemical Technique		Physical Technique	
Suspension	Emulsion	Physico-Chemical	Physico-Mechanical
Polymerization	Polycondensation	Simple Coacervation	Simple Extrusion
In situ/Matrix	Interfacial	Complex Coacervation	Central Extrusion
Interfacial			Spray Drying

2.2 Physical methods

2.2.1 Physico-chemical

Coacervation and in situ polymerization are technologies based on phase separation used for preparing microcapsules. Coacervation is a colloid phenomenon. When a solution of a colloid is in an appropriate solvent, diverse changes can bring about a reduction of the solubility of the colloid. As a result of this reduction a large part of the colloid can be separated out into a new phase, and then the original one phase system becomes two phases [4]. Coacervation may commence in a number of different ways through temperature and changing of pH.

As the coacervate forms, suspended core particles or droplets wets and combines into a continuous coating for the process of microencapsulation to take place.
The final step for microencapsulation is the hardening of coacervate wall and the isolation of microcapsules [4]. There are various methods of preparing microcapsules, other methods are based on physical phenomena and some develop polymerization reactions for producing capsule shell [6]. First systematic approach of phase separation, partial desolvation of a homogeneous polymer solution into a rich polymer phase (coacervate) and the poor polymer phase (medium). There are two types of processes for coacervation, known as simple and complex coacervation.

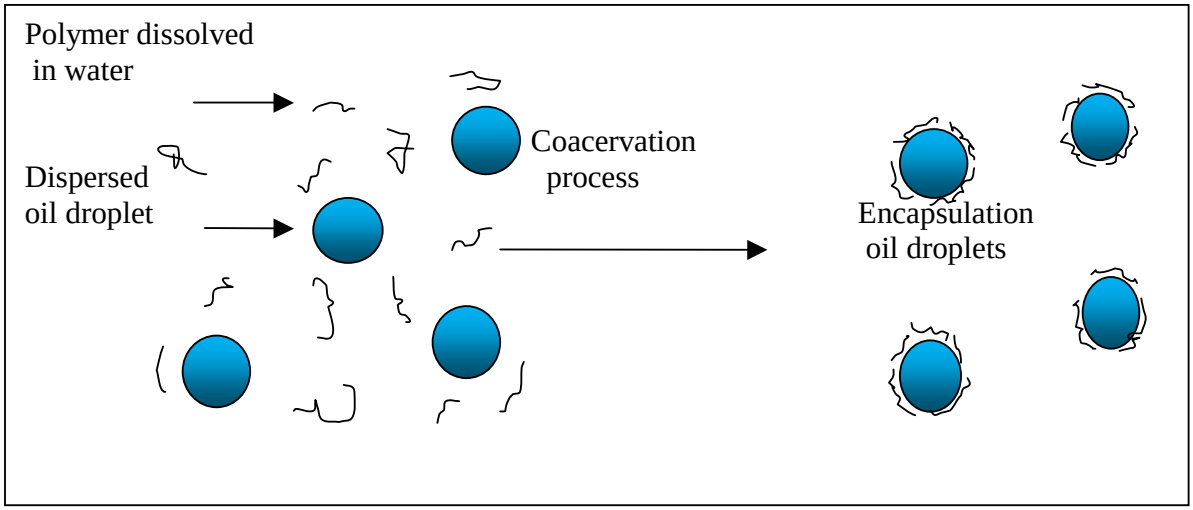


Figure 1: Coacervation process

2.2.1.1 Simple coacervation

In simple coacervation a desolvation agent is added for phase separation, thus the complex involves complexation between the two oppositely charged polymers in a solvent [5].

Three basic steps in complexation are as follows:

- Preparation of the dispersion or emulsion
- Encapsulation of the core
- Stabilization of the encapsulation particles

2.2.1.2 Complex coacervation

Complex coacervation is a very common encapsulation method which produces many applications and regarded as true microencapsulation by means of a chemical process [4]. Complex coacervation method is the interaction of water-soluble polymers with water in forming a liquid and polymer-rich phase. Complex coacervation technology produces single capsules with diameter that ranges from 2-1200 µm and contains 80-90% of the core material.
Most of these capsules have a continuous core and shell structure, while the shell does not have an even thickness. Complex coacervation contains two oppositely charged polymers, joined together forming the complex coacervate and both of these polymers form part of the final capsule shell [6].

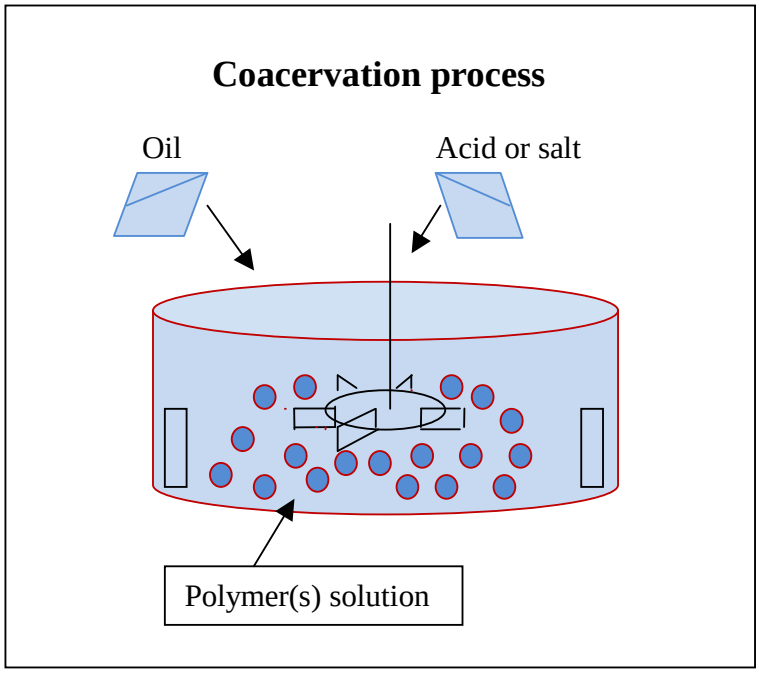


Figure 1.2: Complex coacervation process

The advantage part of this method is the reaction of cationic and anionic polymers [2]. First the core material (oil) is dispersed into polymer solution or cationic aqueous polymer. The second polymer (anionic, water-soluble) solution then added to the prepared dispersion. Deposition of the shell material onto core particles takes place when the two polymers form a complex. This process is generated by change in pH, temperature, ionic strength, molecular weight, and

concentration [4]. Finally, the prepared microcapsules are stabilized by cross linking, desolvation or thermal treatment which hardens the microcapsule wall formed around the core particles. Complex coacervation is used to produce microcapsules containing fragrant oils, liquid crystals, dyes or ink as core material [5].

2.2.2 Physico-mechanical

Mechanical process is one of the methods of microencapsulation; this method is divided into the following subgroup as shown below:

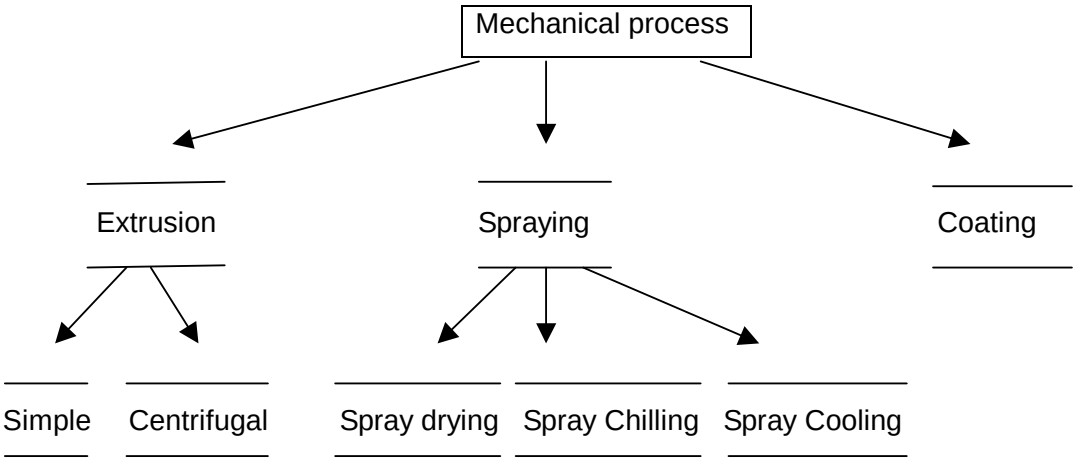


Figure 1.3: Mechanical process of microencapsulation [4]

1.2.2.1 Simple Extrusion

An extrusion device consists of a droplet generator and a hardening bath. The hardening of liquid micro-droplets and their conversion to solid micro-droplets are accomplished by a diversity of mechanisms, including melt solidification, chelation, solvent extraction and evaporation [1].

1.2.2.2 Centrifugal Extrusion

Centrifugal Extrusion is the one of the processes that commonly produces capsules with a large size that ranges from 250 µm up to a few millimeters in diameter [2]. The core and shell material are pumped through a spinning two-fluid nozzle, which produces a continuous two-fluid rod of liquid that breaks up into a flow of spherical droplets as it appears from the nozzle [6].

Liquids are encapsulated using a rotating extrusion head containing concentric nozzles. In this process, the core liquid is surrounded by a sheath of wall solution or melt. As the jet moves through the air it breaks into droplets of core, each coated with the wall solution. While the droplets escape, a molten wall may be hardened or a solvent may be evaporated from the wall solution [3]. Then the droplets fall into a gelling bath where conversion of gel heads takes place. These heads are dried to produce solid shell capsules, and these capsules are suitable for core materials that are water-immiscible oils [6].

2.3 Spray Drying

2.3.1 Brief history of spray drying

The development of spray drying equipment and techniques evolved from the 1870s through the early 1900s. The first known spray dryers used nozzle atomizers, while rotary atomizers was introduced several decades later. Little commercial use of the process was made until the 1920s because of the simple design and practical difficulties in continuous operation. The first major commercial application of the technology was milk drying. Through the next 20 years, new designs were developed to accommodate heat-sensitive products, emulsions and mixtures [7].

2.3.2 Spray drying process

Spray drying has the ability to produce powders containing specific particle size and moisture content [8]. It is a technical method used to dry aqueous or organic solutions and emulsions in industrial chemistry, food industry and textile applications. To date, products such as dry milk powder, detergents and dyes are spray dried products. Spray drying is considered as one of the quickest methods of drying. Spray drying involves moisture evaporation from an atomized feed by mixing the spray and the drying medium (air) [7].

Spray drying serves as a microencapsulation technique when core material is dissolved or suspended in a polymer solution and becomes trapped in the dried particle [3]. The sprayer feed is prepared by mixing the core material with polymer solution using dispersing agents (surfactants). When the spraying of the feed is placed into the hot chamber it produces a

shower of polymer solution containing dispersed active ingredient. The polymer solutions lose their solvent of the hot air which is released simultaneously with the micro-droplets.
The disadvantage of this method is when the polymer solvent is aqueous; the recycling of the solvent and treatment of exhaust air are avoided [1].

Another method is by preparing an emulsion with dispersing the core material either by oil or active ingredient incapable of mixing with water. The emulsion is placed into a concentrated solution of wall material until the desired size of oil droplets are achieved [2]. The emulsion is reduced into a fine spray of droplets which are being pumped through a rotating disc into a heated chamber of a spray drier. Water part of the emulsion is evaporated which leads to dried capsules that varies in shape and containing scattered drops of core material. These capsules are collected through continuous discharge from the spray drying chamber [2].

The spray drying consists of a sequence of four processes:

1. Dispersion of the feed solution

Dispersion can be achieved by different kinds of energy which can be used to separate a solution into fine particles. Higher the energy produces smaller the droplets.

2. Mixing of spray and drying medium

Spray dryer designs plays an important role in the mixing of spray and drying air. The following are different designs of the spray dryer.

- Co-Current flow
- Counter-Current flow
- Mixed flow

3. Open and closed-cycle system

Open-cycle system is when the air flow is heated using a burner or by electricity and the process is exhausted to atmosphere. If the heated air is recycled or reused, then it is a closed-cycle system. This system is mostly used for production of flammable solvents, toxic and oxygen sensitive products [8].

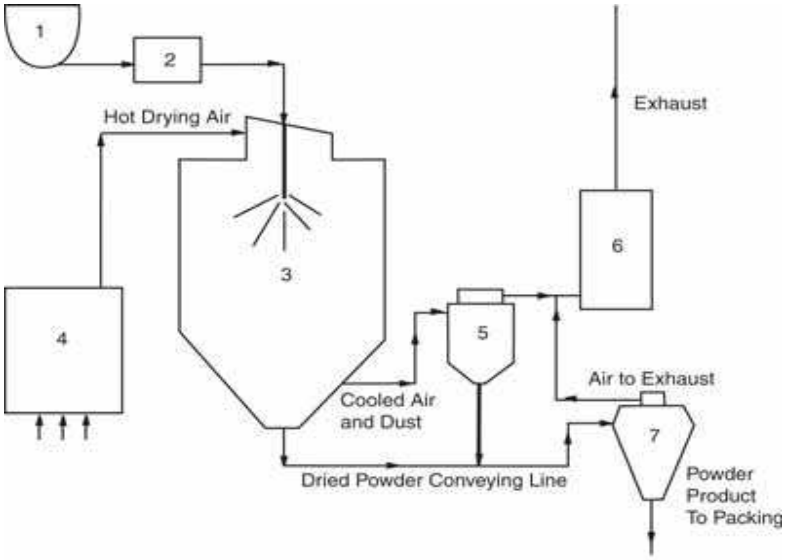


Figure 1.4: Spray drying machine-Open cycle counter-current system

4. Drying of spray

Evaporation takes place when the droplets of the spray come in contact with drying air; saturated film quickly appears on the droplet surface. The evaporation leads to cooling process for the droplet, the droplet passes through the drying chamber for completion of moisture removal. The product must be removed from the dryer before the temperature of the product rises to the outlet drying air temperature [8].

2.3.3 Advantages of spray drying

- In practical use it is designed to meet any required abilities.
- Feed rates ranges from a few pounds per hour to over 100 tons per hour.
- Able to operate with both heat-resistant and heat sensitive products.
- Feedstock can be in solution, slurry, paste, gel, suspension or melt form.
- Product density can be controlled.
- Particles with close to spherical shapes can be produced.
- Material does not contact metal surfaces until dried, reducing corrosion problems [7].

One of the disadvantages of spray drying, when water is a chosen solvent the encapsulation has limitations to the shell materials being soluble in water. Another problem is producing capsules with free or surface core material. This is due to the rapid occurrence of water evaporation from a capsule in the chamber of the spray dryer. Low boiling point compounds with limitations to water solubility cause problem to spray-dry encapsulation [7].

2.3.4 Spray dryer machine

The machine used for spray drying is called spray dryer. Its function is to transport flow of liquid and separate the solution as a solid and the solvent into vapor. The liquid is sprayed through a nozzle into a hot vapor for drying process and the rest is vaporized. The role of the nozzle is to produce small droplets in order to increase the rate of water vaporization and of the heat transfer. Formation of solids takes place as moisture disperses from the droplets. The solid form is then collected in a container which is connected to the cyclone. Depending on the nozzle, the droplet sizes may range from 20 to 180 micrometers. In comparison to other methods of drying, spray dryer is found to be the quickest way of drying products [8].

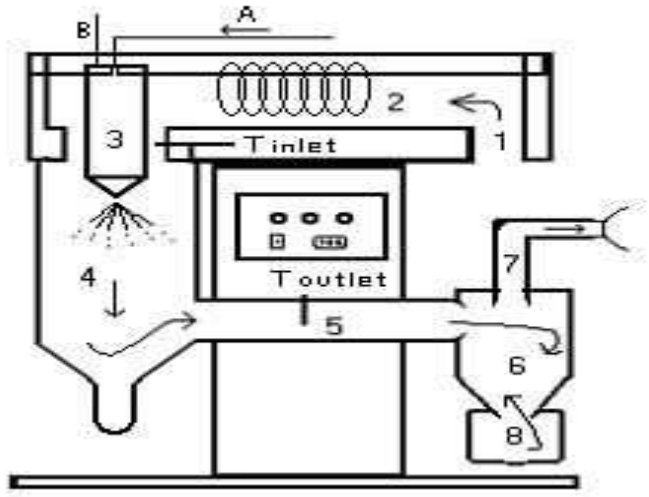


Figure 1.5: Laboratory-scale dryer [10]

A=Solution or suspension to be dried in, B=Atomization gas in, 1= Drying gas in, 2=Heating of drying gas, 3=Spraying of solution or suspension, 4=Drying chamber, 5=Part between drying chamber and cyclone, 6=Cyclone, 7=Drying gas is taken away, 8=Collection vessel of product, arrows mean that this is co-current lab-spray dryer.

2.3.5 Types of spray dryer

2.3.5.1 Co-current flow dryer

The spray and the hot air enter the dryer and both pass through the chamber in the same direction. Co-current dryer is designed for heat-sensitive products, the droplet come into contact with the hot air at highest moisture content [8]. The co-current flow dryer is the type of the dryer that we will be using for the thesis.

2.3.5.2 Counter-current flow dryer

The solution to be dried (sprayed) and hot air enters the dryer in opposite direction at the end of the dryer. The air enters at the bottom and flows upwards while the atomizer is positioned at the top [9]. The product falls downwards and surrounded by hot air into the collection container. The product becomes very hot while the remaining moisture is evaporated [8]. Spray evaporation is more rapid and energy efficiency is higher, this is because there is contact between the dried particles and the hot air. Counter-current dryers usually use nozzles for atomization due to the energy of the spray that can be directed against the air movement. This machine is not suitable for heat-sensitive products, soaps and detergents are most commonly dried in counter-current dryer.

2.3.5.3 Dehumidifier B-296

The Dehumidifier consists of three different applications [8]:

1. Inlet air conditioning
   The drying conditions are clear for removal of water content using a cold trap with $5^{O}C$ temperature.
2. Closed loop with aqueous solutions
   For the use of aqueous solutions with less than 50% organic solvents, additional pre-heat exchanger allows the efficient condensations which results in dry products.
3. Inlet air chiller
   Producing optimal solidification

Table 2: Diameter sizes of microencapsulated techniques by physical methods

Physical methods	Diameter sizes [µm]
Coacervation	2-1200
Solvent evaporation	0.5-1000
Centrifugal extrusion nozzle	250-2500
Spray drying	5-5000

2.4 Chemical methods

2.4.1 Polymerization process

2.4.1.1 Interfacial polymerization

Interfacial polymerization forms capsules that have a continuous core/shell structure and a spherical geometry. Most of the outer surface of these capsules is smooth and uniform. The interior surface of the capsule is irregular and not uniformly deposited around the core [6].
Interfacial polymerization is a chemical technique that is characterized by wall formation that passes through the rapid polymerization of monomers at the surface of particles of dispersed core material. The monomer is then dissolved in the core material and this solution is dispersed in an aqueous phase. The monomer with a reactant is added to an aqueous phase, in which polymerization rapidly follows at the surface of core droplet thus forming the capsule wall [1].

Figure 1.6: Emulsion process

2.4.1.2 In situ polymerization

Microencapsulation is formed of solid core particles by suspension and dispersion polymerizations. The core is embedded or coated by the polymer as it is being formed and this is known as microencapsulation in situ polymerization [2].

In situ polymerization is a chemical technique very similar to interfacial polymerization. The similarities are because the formation of the capsule shell occurs due to polymerization of monomers that is added to the encapsulation reactor [6]. In situ polymerization is different from other polymerization because of the reactants that are not included in the core material [1]. This polymerization is another phase separation complex methodology for microencapsulation. In this method, monomers dispersed in two different phases thus core and suspending medium, combine and co-polymerize upon addition of a cross linker at the interface. With this technique liquids or solids can be encapsulated. It is only applied for very specific core shell-combinations.

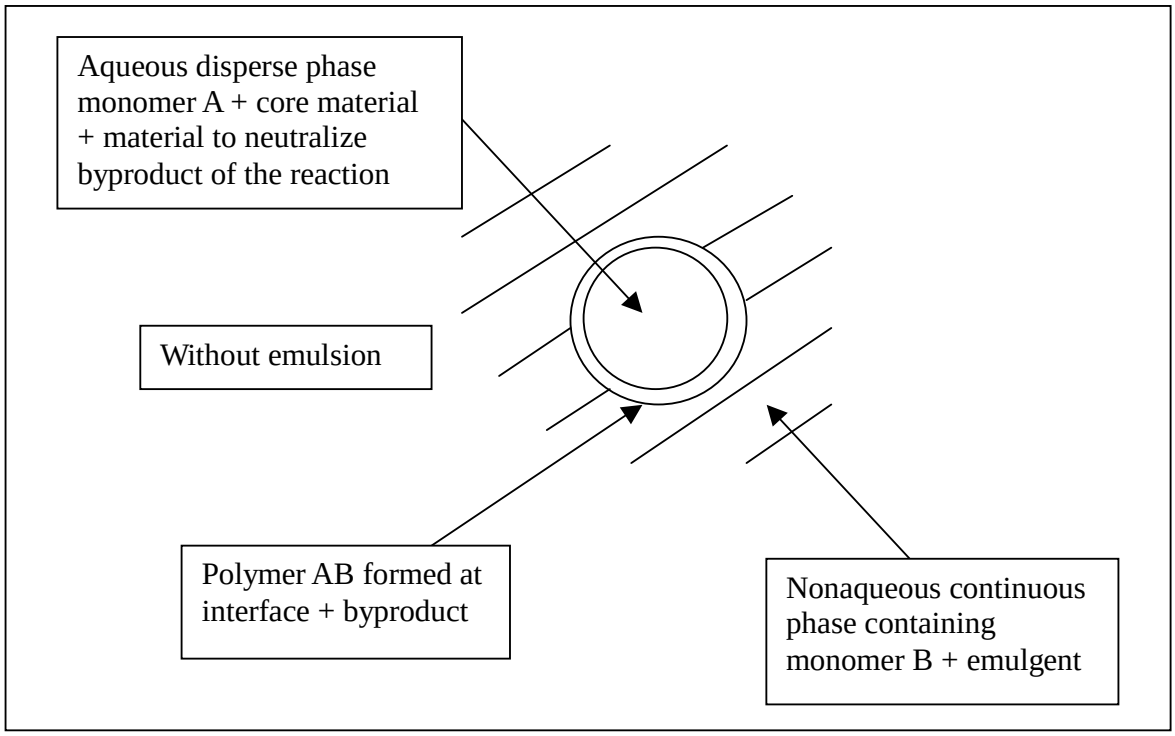


Figure 1.7: Schematic diagram of the in situ polymerization process

2.4.1.3 Matrix polymerization

The core material is imbedded in a polymeric matrix during formation of the particles. A simple method of this type is spray-drying, in which the particle is formed by evaporation of the solvent from the matrix material. However, the solidification of the matrix can also be caused by a chemical change and this is known as matrix polymerization [3]. The matrix type of microcapsules are prepared by suspension polymerization and accomplished by dissolving the core substance in the monomer and then followed by polymerization.

Microencapsulation by emulsion polymerization appears more complicated than the suspension and dispersion polymerization; in this case the monomer is emulsified in the polymerization medium [2]. Suspension polymerization technique is carried out in an aqueous phase containing the stabilizer. The mixture contains the monomer, the cross-linker and the initiator dispersed, and then added into a vessel reactor containing the suspension medium. The polymerization is carried out at elevated temperatures for several hours resulting in polymeric micro-beads obtained by filtration or centrifugation and washing [12].

2.4.2 Polycondensation process

2.4.2.1 Interfacial polycondensation

Interfacial polycondensation involves the polymerization of two complementary monomers in a two phase suspension system. Each of the two complementary monomers resides largely in one of the two immiscible phases in the suspension system [13]. Thus resulting in polycondensate, this is formed at one side of the interface and may be soluble in the droplet phase. Application of interfacial polycondesation can be applied to produce both of mononuclear and matrix microcapsules, and the application depends on the solubility of the polycondensate in the droplet phase [6]. If the polymer is soluble in the droplets, matrix microcapsules are formed thus the particle forming interfacial polycondensation. If the polymer is insoluble in the droplets it forms a membrane around them, and the droplets are thus individually encapsulated by the polymer. This leads to the formation of microcapsules, and hence capsule forming interfacial polycondensation [2].

Table 3: Diameter sizes of microencapsulated techniques by chemical methods

Physical methods	Diameter sizes [µm]
Interfacial polymerization	2-2500
Phase separation	0.5-1000
In situ polymerization	0.5-1000

2.5 Morphology of microcapsules

Morphology depends on form and structure of an organism. Morphology of microcapsules depends mainly on the core material and the deposition process of the shell. Microcapsules consist of a variety of structures, some containing a spherical geometry with a core section enclosed by shell [6]. Microcapsules may have regular or irregular shapes, on the basis of the structure it can be classified as mononuclear, polynuclear and matrix types as shown in figure 2.1.

Mononuclear microcapsules are known as core-shell containing the shell around the core, whereas the polynuclear capsules have many cores enclosed within the shell [13]. Matrix microcapsules, core material are circulated in a uniform structure (composition) into the shell material. Microcapsules can also have mononuclear with multiple shells or may form clusters of microcapsules [5].

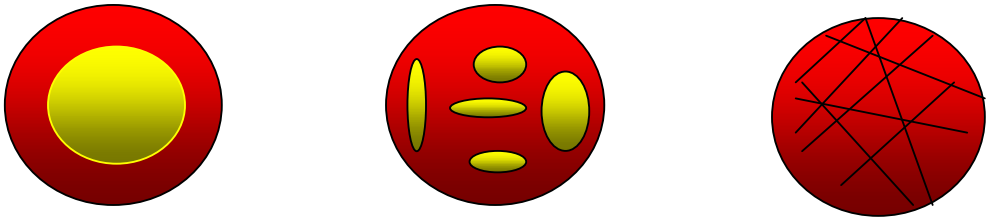


Figure 2.1: Different types of microcapsules [13].

2.6 Types of microcapsules

2.6.1 Polychromic and thermochromic microcapsules

Colour-changing technology has been around for a number of years. New applications are now beginning to be seen in textiles, such as product labeling and medical and security applications. There are two major types of colour-changing systems, thus are thermochromatic which changes the colour in response to temperature, and photochromatic which changes colour in response to UV light. Both forms of colour-change material are produced in an encapsulated form, as microencapsulation helps to protect these sensitive chemicals from the external environment [11].

These technology also contributes to make dyes that change colour at specific temperatures for a given application, for instance when colour changes can be initiated from the heat generated in response to human contact.

Physiochemical and chemical processes such as coacervation and interfacial polymerization have been used to microencapsulate photochromic and thermo-chromic systems. Interfacial polymerization techniques provide durability on textiles and used to produce textile fibers and films such as polyester, nylon and polyurethane. The most widely used system for microencapsulation of thermochromic and photochromic inks involves urea or melamineformaldehyde systems [11]. Microencapsulated thermochromatic dyes generally survive up to 20 laundering cycles, except for excessive drying at elevated temperatures.

2.6.2 Controlled Delivery Microcapsules

2.6.2.1 Release Delivery Mechanisms

There are three types of stimulus released by mechanisms:

- Mechanical
- Chemical
- Thermal

Microcapsules control the release rate of the core by means of controlling the pressure and temperature. For example, an increase in temperature increases the core to break the wall as shown in figure 2.2. There is a period in which the core is slowly released, even if there's no change in pressure and temperature.

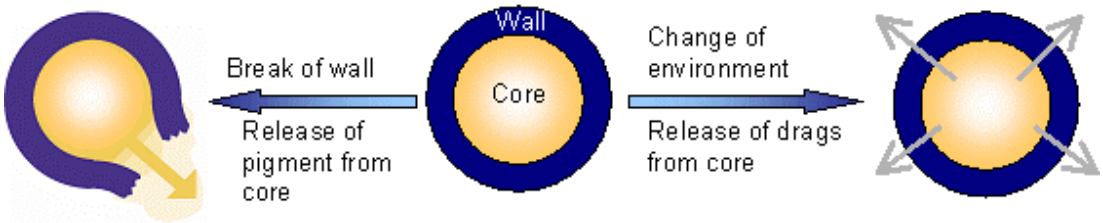


Figure 2.2: Release mechanism

Another mechanism is the release of the shell after degradation, which may be caused by dissolution that is generated by either chemical or enzymatic breakdown of the shell [13]. This release depends on the development of certain environmental state, when it has reached the

state the time of the release can be designed by the variance of thickness and composition of the shell [12].

Generally, the rate of release of microcapsules mainly depends on the structure of the polymer shell, which is influenced by the conditions retained from the preparation. Crystallinity and crosslink density are there characteristics of the shell wall, these walls increases with a significant reduction of the release rate.

The rate of release is commonly expressed as a first-order rate process.

$$kc=-dc/dt$$

K is the diffusion constant and c is the concentration gradient

2.7 Fixation of microcapsules to textiles

The microcapsules are applied to the fabric using a binder (e.g. acrylic) as shown in figure 2.3. In some cases, nylon and gelatine microcapsules, ionic interaction can create extensive binding. The use of binders has some disadvantages, there should be enough amounts for a good fixation of the microcapsules but it should not disturb the release. A microcapsule covered with binder may be harder to break or the binder layer may prevent the release from the fabric after the microcapsule has been broken. Binders can also cover the surface properties of the fibers in the fabric. To increase the use of microcapsules as controlled delivery vehicle for textiles, microcapsules with reactive shells that bond covalently to the fibers should be developed. The reactive groups can be based on those used in dye molecules. The choice is not unlimited because the microcapsules should be able to withstand the conditions necessary for the binding reaction to occur [11].

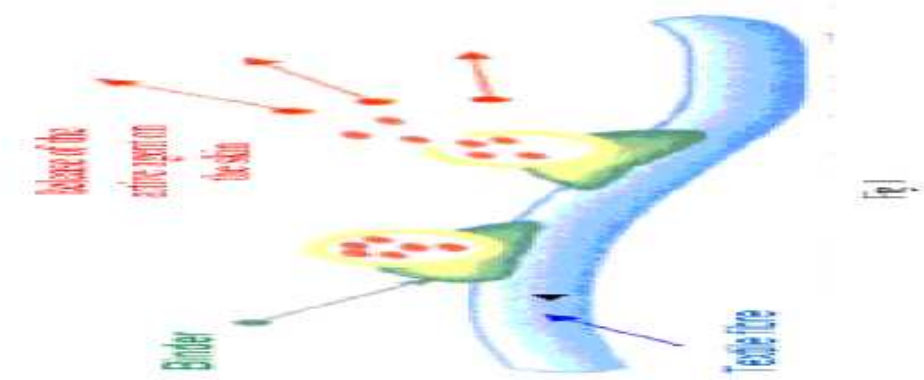


Figure 2.3: Fixation of microcapsule and a binder on textile fiber

2.8 Main reasons for microencapsulation

2.8.1 Advantages

- Protection of unstable, sensitive materials (reactive compounds) against surrounding environment
- Keeping incompatible substance separate from other components of products
- Better processability, thus improving solubility, dispersibility and flowability
- Prevention of degradative reaction (oxidation, dehydration)
- Safe and convenient handling of toxic materials
- Masking of odor, taste or even reducing toxicity of core component due to its isolation
- Increasing stability of the core material (against heat moisture, oxidation or reduction light)
- Changing the volume and density (conversion of liquids into fine powder)
- Controlling or delaying the release of core material thru surrounding shell. The release is ensured by various mechanisms, which are as follows:
  a) Mechanical rupture of capsule wall
  b) Dissolution of the wall
  c) Melting of the wall
  d) Diffusion through the wall
  e) Slow erosion of shell and biodegradation [12]

2.8.2 Disadvantages

Micro-encapsulation is used as a means of improving durability of chemical finishes or for gradual release of chemicals such as fragrances and anti-microbial chemicals. Finishes of microencapsulation and applied to garments may be resistant to many machine washes.
Complexity and slowness of the reaction in chemical methods (interfacial polymerization) and unwanted side products are produced.
When microcapsules are applied to the textile material without binder, promotes increased adherence of microencapsulation in textile [5].

2.9 Microencapsulation technology

2.9.1 Control Release

Controlled or targeted release is the most common application of microcapsules. Most microcapsules are exceptionally stable and display great retardation of the encapsulated substances. These substances can either be released at once or if the shell material is dissolved. The control release is disturbed when a less amount of binder is used which also affect the fixation process [12].

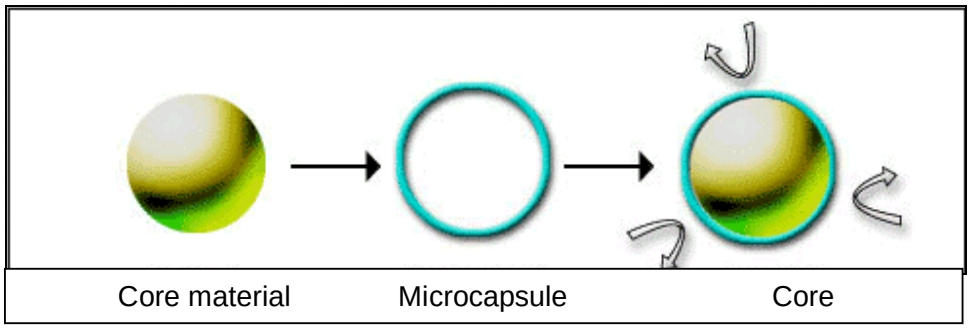


Figure 2.4: The formation and release of the capsule

2.9.2 Protection

Microcapsules are also used to temporarily store unstable substances. These capsules contain active agents that are not appropriate for their usage, due to various reasons which includes low

solubility, reactivity and low stability. Microcapsules prevent the early loss of active ingredients which is reflected by the weakness of its activities [12].

Microencapsulation is an effective method of protecting unstable or reactive products against outside influence such as oxidation, alkalinity, acidity, heat, polluting gases, moisture and evaporation. Microencapsulation also prevents undesirable interactions between the active agents and other components in the system, therefore increases their washing durability. Microencapsulation may also be used to cover and prevent the release of unpleasant odor during manufacturing process [12].

2.9.3 Compatibility

The active products are permanently encapsulated in order to allow a mixture of inconsistent products. Protection and compatibility are both connected in various applications, for example phase-change materials (PCM) which are permanently involved in their encapsulated forms [12].

The following are the characteristic of compatibility:

- The conversion of liquids into powders thus to improve mixing and compounding.
- The improvement of handling of active agents before processing.
- Protection of workers and end-users against exposure to hazardous or other toxic substances.

2.10 Phase change material

Material that go through the phase change process are known as phase change material. This material was developed during the 1970s by the National Aeronautical and Space Administration (space research program) for US spaceflight division [12]. Phase change material (PCM) is a substance that contains high heat of fusion, where melting and solidifying process takes place at a certain temperature. Phase change material is capable of storing and releasing large amounts of energy and classified as latent heat storage (LHS) units. The latent heat storage is characterized into four different phase changes, which are solid-solid, solid-liquid, solid-gas and

liquid-gas phase change. The most commonly used phase change is the solid-liquid change. Solid-solid phase changes are known to be very slow and for the low heat transformation. Liquid-gas phase change are not used in practical procedures for thermal storage, they require large volumes to store materials in gas phase [14].

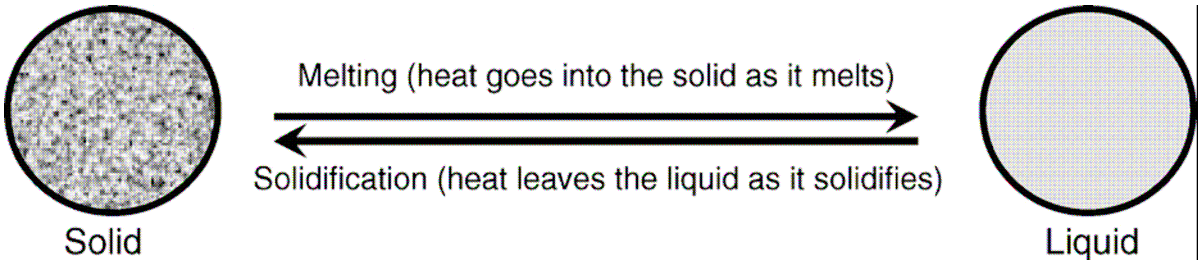


Figure 2.5: Schematic representation of phase change process

2.10.1 Solid-liquid phase change

The phase change material absorbs heat at a constant temperature while the material is transformed to liquid phase. When the temperature decreases around the liquid material, solidification takes place around the material and releasing the stored latent heat. The melting temperature of a typical phase change material is between 0-250ºC. Unlike conventional storage materials, when PCMs reach the temperature at which they change phase (their melting point) they absorb large amounts of heat without getting hotter [14].

2.10.2 PCM properties

Phase change material is characterized into the following properties:

- adjust to all types of environment
- high heat of fusion, high specific heat, high density
- melting temperature in desired temperature range
- small volume change during phase change
- complete reversible freeze or melt cycle
- chemical stability, non-corrosive, non-poisonous
- non-toxic, non-flammable and non-explosive material

2.10.3 PCM in textile material

During heating process, the textile materials absorb heat while there's a constant rise in temperature. The heat is stored in the material and released into the environment through a reverse cooling process. During the cooling process, the material temperature decreases continuously. Textile material absorbs about 1 kJ/kg of heat while its temperature rises by one degree Celsius [17].

Phase change material absorbs approximately 200 KJ/kg of heat during melting process. The temperature of the PCM and its surrounding area remains constant, during the complete melting process [17]. The high heat transfer during the melting and crystallization process proves that PCM can serve as a source of heat storage. Phase change material stores, absorbs and releases heat in various changing temperature. This material is mostly applied in the production of smart textiles.

2.10.4 PCM as hydrocarbons

Phase Change Materials are waxes that have the distinctive capacity to immerse and release heat energy without change in temperature. These waxes include eicosane, octadecane, nonadecane, heptadecane and hexadecane. Waxes are hydrocarbons or esters of fatty acids that are insoluble in water but soluble in nonpolar organic solvents [15]. Waxes are monoesters of fatty acids and fatty alcohols. They are usually distinguished from fats because fats are triesters of glycerin. Both fats and waxes are esters of fatty acids. Waxes can be produced by marine animals; another source of wax is vegetable sources. These sources are solid or semi-solid substance because they contain a high molecular weight and high percentage of saturated hydrocarbons [15]. Typical transition temperature of waxes range from 15 to 30^{O}C [15].The melting point of waxes is above 45^{O}C and has a relatively low viscosity when melted. When then wax melts, the molecular bonds of waxes are loosened through absorption of thermal energy. The thermal energy is released when the wax hardens and when its molecular bonds are reformed [15].

2.10.5 Characteristics of PCM

In terms of classification, there are four general categories of phase change materials:

- Salt Hydrates (Na_2SO_4, $CaCl_2$)
- Eutectic Salts
- Paraffin's
- Non-Paraffin Organics

Table 4: Characteristics of phase change material

PCM	Material	Advantages	Disadvantages
Organic	Waxes Polyethylene glycols	No segregation Chemical stable High heat of fusion Safe and non-reactive	Cost is high Lower latent heat/density Can be flammable Wide melting range Lower heat transfer
Salt hydrates	Na_2SO_4 $CaCl_2$	Low cost Non-flammable Good heat transfer High heat of fusion Sharp melting point	Change of volume is very high Need careful preparation Need additives to stabilize Prone to supercooling

The most popular phase change material used in textile applications are based on paraffin waxes. Paraffin wax is obtained from a mixture of solid hydrocarbons derived from petroleum. Paraffin wax has a melting point that ranges from $47^{O}C$ to $64^{O}C$. It is insoluble in water, but soluble in ether, benzene, and certain esters. Paraffin wax is an excellent material for heat storage, having a specific heat capacity (2.14-2.9 J/g.K) and a heat of fusion (200-220 J/g) [14]. Paraffin wax has high heat storage capacities compared to other phase change materials.

In addition, paraffin can be mixed in order to realize desired temperature ranges in which a phase change takes place [12]. The main disadvantages of paraffin based PCM are as follows; less thermal capacity, low density and lower thermal conductivity both in solid and liquid phases.

2.10.6 Encapsulation process

The PCM was introduced to encapsulation process in finding ways to improving the construction material. Others reasons for encapsulation were to hold the liquid phase of the PCM, and to avoid contact with the environment, for protecting. Encapsulation is usually classified as either macro- or microencapsulation [12].

2.10.6.1 Macro-encapsulation

Macro-encapsulation was one of the encapsulation methods that were used previously. This method was unsuccessful due to low thermal conductivity of the material [15]. The process of macro-encapsulation took place when heat was absorbed from the liquid phase; the phase change material solidified around the edges and prevented effective heat transfer.

2.10.6.2 Microencapsulation process

Microencapsulation is the process of capturing small amounts of phase change materials (core) in a shell material (capsule wall) so that the phase change materials are permanently enclosed and protected [17]. The protective polymer shell is very durable and designed to withstand textile production methods used in fiber, yarn spinning, weaving, knitting, and coating applications. Microencapsulation also allows the phase change materials to be incorporated simply and economically into conventional construction materials [15]. Microencapsulation gives a softer hand, greater stretch, more breathability and air permeability to the fabrics.

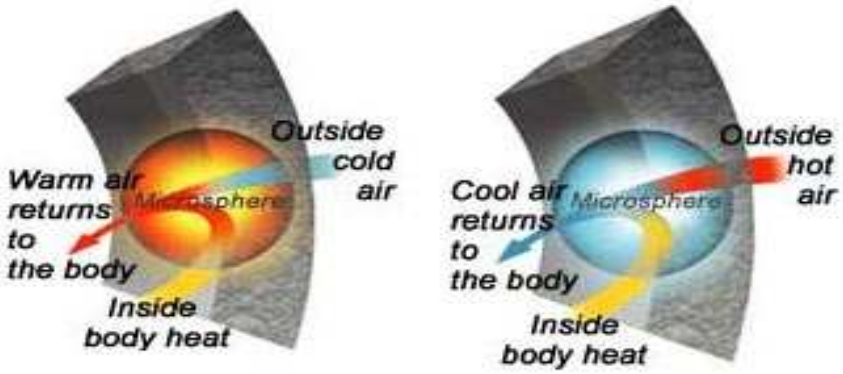


Figure 2.6: Materials work by absorbing excess heat, storing and returning the heat.

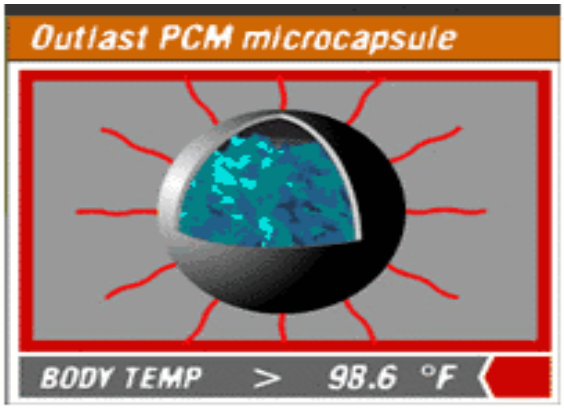
The microencapsulation process and the size of the particle affect temperatures. The particle with smaller size gives a greater difference between the melting and freezing temperatures of PCM. Capsules with small size provide a large specific surface area for heat transfer. Common particle sizes of wax based PCM ranges from 3 to 10 µm or smaller. The core contains 80-85 % of the volume of particles, and the outer shell is around 1 µm thick [12].

Micro-encapsulated PCM can be applied on woven, nonwoven or knitted fabrics. The capsules that formed from microencapsulation process are added to the fabric in various ways. The PCM microcapsules are permanently fixed within the fibre structure during the wet spinning process of fibre manufacture [16]. PCM is also used as a method of thermoregulation in many textile products such as clothing, interlining and technical textiles [12].

There are various ways of applying PCM microcapsules on a finished fabric, the application entails fixation of microcapsules in a fabric using coating compounds like acrylic and polyurethane. Coating methods which are used for this application are knife-over-roll, knife-over-air, pad-dry-cure, gravure, dip coating and transfer coating. Another application is by foam dispersion, microcapsules are mixed into a water-blown polyurethane foam mix and these foams are applied to a fabric in a lamination procedure, where the water is removed from the system by the drying process [17].

2.10.7 Effects on fabrics

The effect of PCM on fabrics during heating process, when the fabric absorbs heat energy as it moves from a solid state to a liquid state during melting process. This phase change produces a short-term cooling effect in the clothing layers, in which the heat energy may be coming from the body temperature or warm surroundings [18]. The actual temperature of the phase change in fabrics should be close to the body temperature.



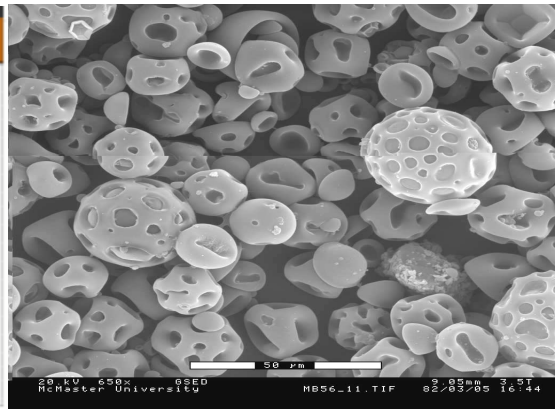


Figure 2.7a: PCM Skin temperature Figure 2.7b: Microscopic view of PCM

The clothing layer(s) consisting of PCMs have to go through the transition temperature range before the phase change of the material and should either produce or absorb heat. PCMs are transient phenomena; they have no effect in steady state thermal environment [18].

There are several characteristic in encapsulating PCM:

- The material of the container wall must be compatible with the PCM
- The container wall has to be sufficiently thick for assurance of tension in diffusion
- Encapsulation must be able to cope with the mechanical stress on the container walls caused by volume change of the PCM [14]

Table 5: Applications of micro-encapsulated PCM [14]

Applications	Product end user
Textiles	Medical textiles, furniture coverings, mattresses, military uniforms
Building Materials	Wall board, paint, insulation, tiles, flooring and roofing
Apparel	Elegant fleece vests, men and women hats, gloves and rainwear
Sports Wear	Apparel jackets and jacket linings, boots, running shoes, socks and ski and snowboard gloves.
Environmental	PCMs can be used in conjunction with solar heating and radiant heat flooring as a latent heat storage device.

Phase change materials are also used in freezers packs, protective clothing and hard hats designed to keep people cool in hot environments. One of the most important recent breakthroughs with PCMs is in the building industry [15].

2.11 Bicomponent fibers

2.11.1 General Introduction

Bicomponent fibers (conjugate fibers) are fibers that are made from a process in which two polymers are extruded from the same spinneret, in which both polymers are contained on the same filament [21]. Bicomponent fibers is based on one component which is usually polyethylene terephthalate (PET) and the other component a co polyester, or both components are copolyesters distinguished by different contents of co-monomers. Processes that take place in the production of bicomponent fibers are based on heat setting at temperature above 200^{O}C and on crystallization of fibers before drawing [19].

Bicomponent fiber consists of two polymers of different chemical or physical properties and thus possesses different extendibility characteristics. Depending on the characteristics of the two polymers, the fiber provides functional properties such as thermal bonding, unique cross section and achieves special polymers or additives for surface adhesion and ultraviolet protection [21].
Bicomponent fibers provide for the possibility of developing the crimp in the finished textile product. The latent crimp, based on the different shrinking power of the two fiber components, will be developed during thermal treatment of the product [19].

2.11.2 Preparation of bicomponent fibers

Bicomponent fibers are prepared by mixing two or more polymers in melted form before or after the spinning nozzle. These fibers consist of homogeneous or heterogeneous mixtures of different homopolymers or copolymers [19].
There are three basic types of bicomponent fibers which are side by side (S/S) type, core/sheath (C/S) type, matrix/fibril (M/F) type as shown in figure 2.13. The two different polymer components inconsistently do not differ in chemical nature. They can differ only in physical parameters such as molecular weight [21].

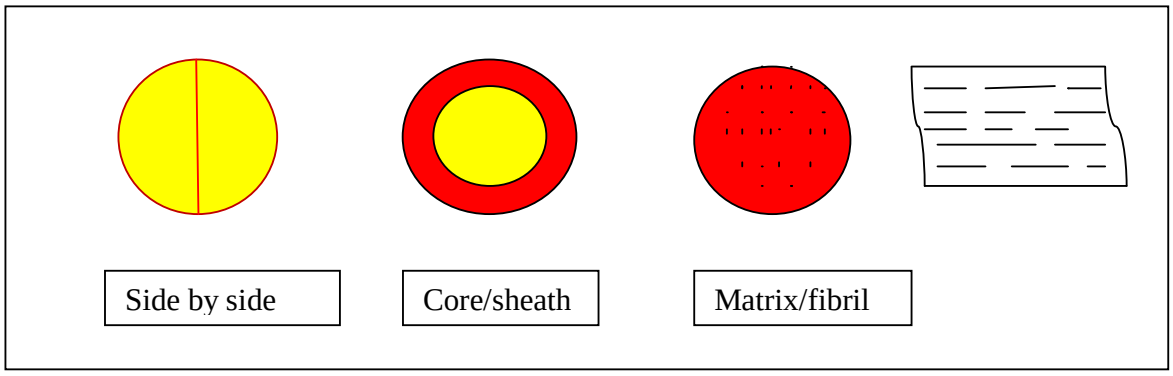


Figure 2.8: Cross sectional form of bicomponent fibers

2.11.3 Classification of bicomponent fibers

2.11.3.1Side-side bicomponent fibers

Bicomponent fibers of side by side type are produced by joining two flows of polymer melt in the spinning nozzle [19].Side by side consist of two components which are divided by length into two or more sections. Adhesion takes place within the two components. Side-by-side fibers are generally used to produce self-bulking fibers and for production of textured yarns with latent crimp [20]. Two PET polymers of different molecular weights produce a self-bulking fiber after relaxing because the two spun birefringences will differ. The relaxed yam will curl up and a spiral crimp will result. A self-bulking fiber can also be made by co-spinning PET with PET co-polyester containing a branching agent in a side-side configuration [21].

2.11.3.2 Core-sheath bicomponent fibers

Bicomponent fibers of core/sheath type are produced using special spinning nozzles capable of enveloping a melt jet forming the core, with a melt flow forming the sheath of the fiber [19].
The core/sheath type contains one components (core) which is fully surrounded by the second component (sheath), adhesion is not essential in this type of fibers [20].
The core-sheath (c/s) configuration is very adaptable because many different polymers may be applied as a sheath over a solid polyester core, thus giving a variety of modified surface properties while maintaining all the major fiber and textile properties of PET.
A widely used c/s heterofil has a normal PET core with a lower softening-point sheath polymer.

When such fibers are laid randomly in a non-woven structure and heated to a temperature above the softening point of the sheath polymer, the fibers will adhere wherever they cross and touch. This process may be done either by heated calendar rolls or simply in a forced draught hot air oven [21].

2.11.3.3 Matrix fibril bicomponent fibers

Bicomponent fibers of the matrix/fibril type are produced from a melt prepared by mechanical mixing of two different melts or by dispersing fibrils of one polymer in the melt of the other polymer [19]. These fibers are spun from the mixture of two polymers in the required proportion; where one polymer is suspended in droplet form in the second melt [20].
One of the examples of matrix/fibril type is a fiber is based on polyethylene terephthalate (PET) fibrils embedded in a matrix of Nylon 6.
The presence of PET fibrils increases the modulus of the fiber, reduces moisture regain and dyeability, improve the texturing ability and give the fiber a unique lustrous appearance [20].

2.11.4 Copolyester fibers

Copolyester is formed when modifications are made to polyesters, which are combination of diacids and diols. When introducing other diacids or other diols to the polyester polyethylene terephthalate (PET), the material becomes co polyester due to its comonomer content [21].
Copolyesters containing high comonomer content ranging from 10 to 40% are used as the low-melting-point component. These fibers are recommended as suitable comonomers such as dicarboxylic acids (such as adipic, isophthalic, naphthalene dicarboxylic acids).Copolyester fibers are capable of improving dyeability on continuous dye ranges and having improved recovery from compression [19].
Copolyesters retain their strength and other mechanical properties regardless of being exposed to a variety of chemicals that usually affect other materials. The most common properties of co polyester are its toughness, versatility and chemical resistance [21].

2.11.4.1 Preparation of co polyester

The preparation of the most common modified polyester fibers are by copolycondensation. The preparation process includes the production of either a statistical copolymer or a block and branch copolymer. Statistical copolymer is prepared by adding two-function comonomer (diol or dicarboxylic acid) during the first phases of re-esterification. Block copolyesters are divided into two groups; first group contains copolymers formed from two types of polymer. One polymer with both ends must be capable of reacting with one end of the other type of polymer [19]. Condensation of the two polymers results in the formation of copolymers of the first group, with this groups exchange reaction does not take place. Second group of block copolymers is obtained when two polymers melt simultaneously with an exchange reaction taking place. Extensive melting time reduces the blocks and forms statistical copolymer.

2.11.4.2 Chemical composition of copolyester fibers

Non-modified PET fibers are prepared from terephthalic acid (or dimethyl terephthalate) and ethylene glycol. In the first phase of the classical method bis(hydroxyethyl)terephthalate is prepared, which is then heated in a vacuum to 260 to 280℃ to give a trans-esterification reaction of polyethylene terephthalate.

The effect of side reactions, about 1.5 to 3% of diethylene glycol (DEG) is always produced:

$$HO\text{-}(CH_2)_2\text{-}0\text{-}(CH_2)_2\text{-}0H$$

Diethylene glycol is introduced into the chains as a statistical copolymer. A more substantial DEG formation takes place especially when the copolymer is prepared with a sodium salt of 5-sulphoisophthalic acid. Owing to the presence of an ether linkage, DEG will increase the sensitivity to photodegradation and degradation by thermo-oxidation [19].

Theoretically, polyethylene should contain hydroxyl (-OH) end groups only. Carboxyl (-COOH) end groups are also produced during various degradation reactions, such as hydrolysis, thermal oxidation, which takes place during polycondensation or melting of PET.

2.11.5 Polyester Fibers

2.11.5.1 Basic Principles of Polyester Fiber

Polyester fibre is a man-made fibre in which the fibre forming substance is any long chain synthetic polymer [21]. Polyester fibers are polymers which contain the ester functional group in their main chain. The most common polyester for fibre purposes is poly (ethylene terephthalate), or simply PET. Polyester is made by reacting ethylene glycol with either terephthalic acid or its methyl ester in the presence of an antimony catalyst [22]. The reaction is carried out at high temperature and vacuum to achieve the high molecular weights need to form useful fibres. Polyesters include naturally-occurring chemicals, such as synthetics through step-growth such as polycarbonate and polybutyrate. Polyesters as thermoplastics may change shape after the application of heat. While combustible at high temperatures, they tend to shrink away from flames and self-extinguish upon ignition [22]. They are strong, lightweight, easily dyeable and wrinkle-resistant and have very good wash-wear properties [21].

2.11.5.2 Polymer formation

Polyethylene Teraphthalate (PET) is a condensation polymer and is industrially produced by either terephthalic acid or dimethyl terephthalate with ethylene glycol.

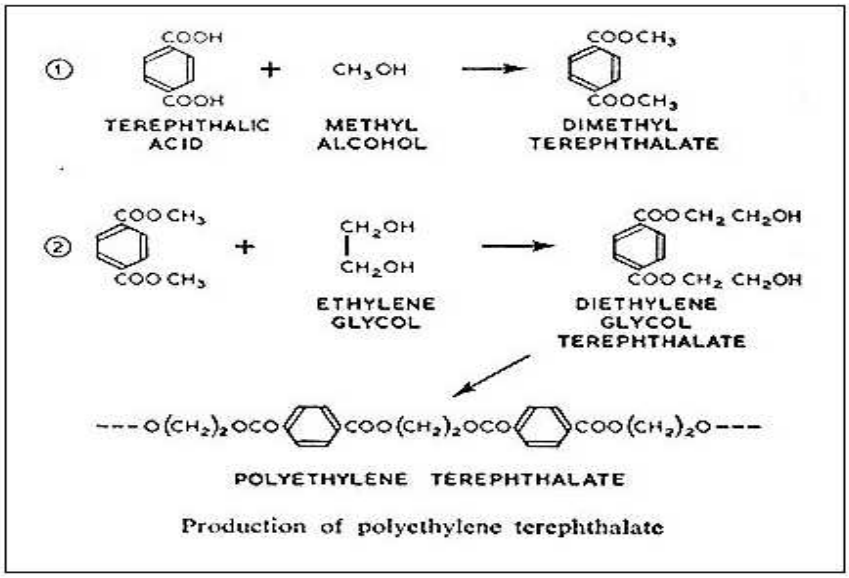


Figure 2.9: Production of polyethylene terephthalate

2.11.5.3 Fiber formation

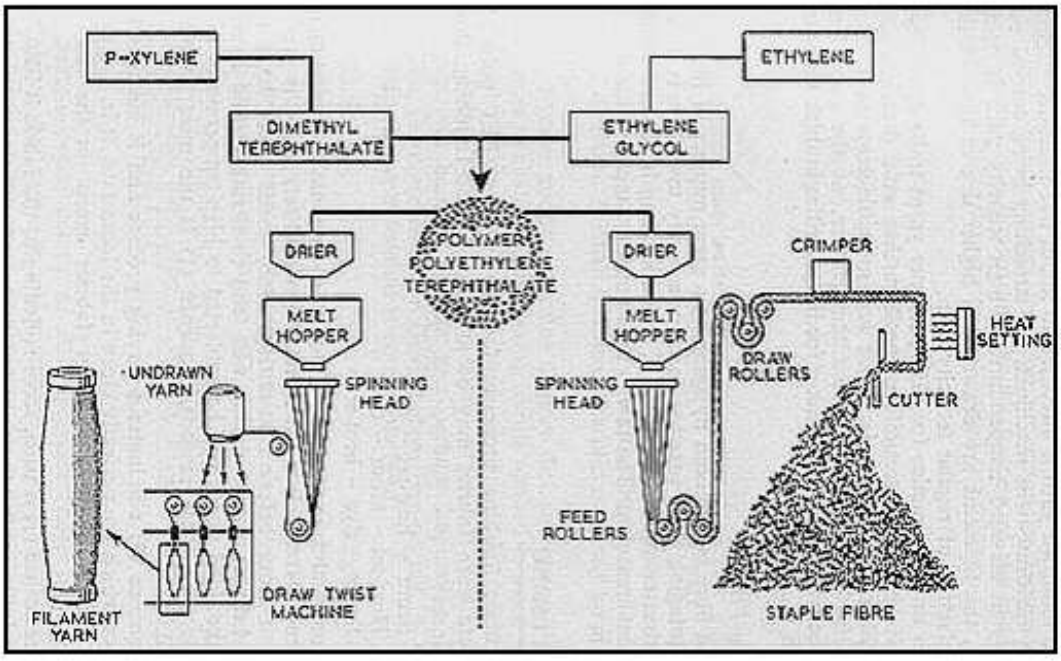


Figure 2.10: Polyester fiber formation

2.11.5.4 Structural composition of PET

Typical PET has 50% crystallinity. The repeat unit of PET is 1.075 nm and is slightly shorter than the length of a fully extended chain (1.09 nm). Therefore, the chains are nearly planar. Another factor for crystallization is the position of the benzene rings. If benzene rings are placed on the chain axis, then close packing of the molecular chains eases polymer crystallization [23].

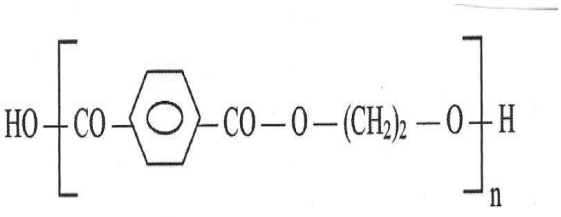


Figure 2.11: Chemical structure of polyester fibre

2.11.5.5 Molecular structure

Polyethylene-terephthalate chains are linear, and there is a frequent exchange between the parts of terephthalic acid and ethylene glycol. When the chains are turned around, the ($-CH_2-CH_2-$) bond results in the formation of two conformers, a planar trans-conformer and a spatial gauche-conformer. Trans-conformation corresponds to the arrangement on the longest elementary unit (1.072 nm). It is the state at which the so-called van der Waals' distances are maintained between the chains and the individual groups in the chains [19].

2.11.5.6 Supramolecular structure

In polyethylene-terephthalate fibers, the microfibril thickness is around 10 nm and the length is around 1 µm. Microfibrils are thin, with a long structure of oval cross-section. The majority of disturbances in microfibrillar amorphous regions are caused by gauche-conformers, which can reversibly transform into trans-conformers [19].

The individual microfibrils are composed into bundles (fibrils) and the fibrils are interconnected by interfibrillar chains. Inadequate arrangement of fibrillar bundles results in the structure containing interfibrillar amorphous region. This fibrous structure is the result of plastic deformations taking place during fiber drawing.
In PET fibers it is formed when the draw ratio is greater than about 2 to 3. The interfibrillar has been found to have an influence in the absorptiveness and mechanical properties of PET fibers.

2.11.5.7 Chemical Properties

Polyester fibers have good resistance to weak mineral acids, even at boiling temperature, and to most strong acids at room temperature, but are dissolved with partial decomposition by concentrated sulfuric acid. Polyester fibers exhibit very good resistance to weathering and are relatively stable even at high temperatures. But under extreme conditions various degradation processes will take place, such as hydrolysis, thermal destruction and photo-degradation. These processes reduce the length of the polymer chains [19].
Polyesters are highly sensitive to bases such as sodium hydroxide and methylamine, which serve as catalysts in the hydrolysis reaction. This susceptibility to alkaline attack is sometimes

used to modify the fabric aesthetics during the finishing process. The porous structures produced on the fiber surface by this technique contribute to higher wettability and better wear properties [23].

Polyester displays excellent resistance to oxidizing agents, such as conventional textile bleaches, and is resistant to cleaning solvents and surfactants. PET is both hydrophobic and oleophilic. The hydrophobic nature imparts water repellency and rapid drying. Polyester fibers have a low moisture regain of around 0.4% under normal conditions. The low moisture content, however, can lead to static problems that affect fabric processing and soiling.

2.11.5.8 Mechanical Properties

An increase of molecular weight further increases the tensile properties, modulus, and elongation. The fibre strength decreases as the degree of arrangement of the chain folds in crystallites rises, and related to the distribution of relative molecular masses and to the orientation of molecular chains.

Elastic recovery in modified PES fibers was found to be affected by the conditions of thermal treatment rather than by the presence of comonomers. The elastic recovery is closely related to the orientation in the amorphous phase after thermal treatment [23].

PET shows nonlinear and time-dependent elastic behavior. It recovers well from stretch, compression, bending, and shear because of its relatively high initial modulus.

Extensional creep occurs under load, with subsequent delay in recovery upon removal of the load. But compared with other melt-spun fibers, the creep is small.

2.11.5.9 Thermal properties

The amorphous phase can be influenced by the presence of a comonomer, and mobility of the amorphous phase is indicated by the glass transition temperature Tg. The amorphous and crystalline contractions are two basic mechanisms leading to macroscopic shrinkage in co polyester fibers. Oriented PET fibers have half-time of crystallization shorter than 0.01 s [19]. The glass transition range is usually in the range of 75^{o}C; crystallization and melting ranges are around 130^{o}C and 260^{o}C, respectively [23].

2.11.5.10 General Polyester Fiber Characteristics

- Strong
- Resistant to stretching and shrinking
- Resistant to most chemicals
- Quick drying
- Crisp and resilient when wet or dry
- Wrinkle and mildew resistant
- Abrasion resistant
- Retains heat-set pleats and crease
- Easily washed

2.11.5.11 Effect of modification on the crystalline phase

The polymer chains are usually arranged in folded form in the crystalline phase. The presence of a comonomer influences the rate of crystallization as well as the size, shape and uniformity of the crystalline structures.

The rate of crystallization is influenced essentially by factors such as

- temperature
- relative molecular mass
- comonomer content
- orientation of chains in amorphous regions

The length of the crystalline unit is 2.12 nm, which is more than double the unit length of PET, the latter being 1.075 nm [19].

2.11.5.12 Effect of modification on the amorphous phase

The chain mobility in amorphous regions can be obtained from glass transition temperature (Tg). The values of glass transition has an influence on the mobility on the amorphous phase, the lower the values of Tg the lower there is a barrier mobility in the amorphous phase.
The effect of the growth of crystallinity is more complicated; a large number of small crystallites are formed at low proportions of the crystalline phase and restrict the mobility of chains with an

increase in Tg. Large crystallites starts to be formed as soon as the amount of the crystalline phase exceeds a certain limit. This process has an influence in the improvement of dyeability of PET fibers after heat-setting at temperatures of about 190℃, when the crystallites become coarser [19].

2.12 Sodium chloride

Sodium chloride it is a white crystalline solid, also known as common salt, table salt. These white crystals are readily soluble in water and saturated solutions boil at 107^{O}C. This chemical compound is known by the formula of NaCl.

Ionic compounds

Sodium chloride is an ionic compound because it consists of oppositely charged ions. The metal ions are positively charged and non-metal ions are negatively charged, and sodium chloride consists of sodium ions Na^{+} and chloride ions Cl^{-}. Thus the formula of NaCl shows that sodium chloride consists of equal numbers of sodium and chloride [24].

The metallic element sodium combines with non-metallic element chlorine to form the ionic compound sodium chloride:

2NaCl (s) + Cl2 (g) ⟶ 2NaCl (s)

2.12.1 Structure of sodium chloride

Sodium chloride forms crystal with cubic symmetry. The crystal structure of sodium chloride, each atom has six nearest neighbours with octahedral geometry. In these, the larger chloride ions shown to the right as green spheres are arranged in a cubic closed packing while the smaller sodium ions, shown to the right as silver spheres, fill all the cubic gaps between them. Each ion is surrounded by six ions of the other kind as shown in figure 2.12 [25].

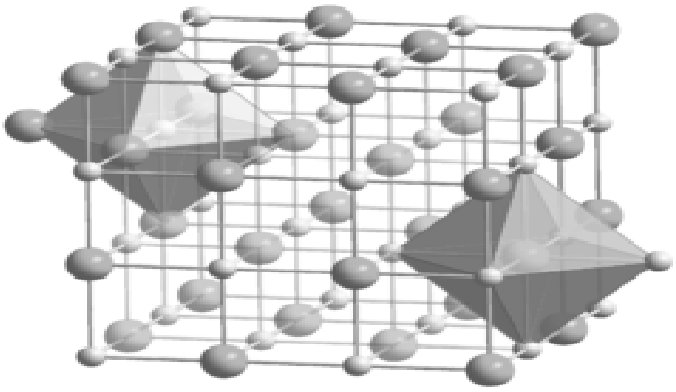


Figure 2.12: Crystal structure of sodium chloride

Sodium chlorine is an electrolyte that has been fused to a liquid by heating. Although crystalline sodium chloride is a poor conductor of electricity, fusing it mobilizes the sodium and chloride ions, which become charge carriers and allow conduction of electric current. Sodium chloride normally melts at 804℃, but the mixture can be kep t liquid at temperatures around 600℃.

The anode reaction is:

$2Cl^- \rightarrow Cl_2 + 2e^-$

The cathode reaction is:

2Na+ + 2e– → 2Na

for an overall reaction of

$2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$

2.12.2 Solubility of sodium chloride

Many ionic solids are soluble in water - although not all. It depends on whether there are big enough attractions between the water molecules and the ions to overcome the attractions between the ions themselves. Positive ions are attracted to the lone pairs on water molecules and coordinate bonds may form. Water molecules form hydrogen bonds with negative ions. There are strong electrostatic attractions between the positive and negative ions, and it takes a lot of heat energy to overcome them. Ionic substances all have high melting and boiling points.

2.12.3 Application on textiles

Sodium chloride is commonly used in water softeners to remove the hardness from water in homes and businesses [3]. Salt is also used as an addition in dyeing, especially with substantive dyes to increase the rate of dye exhaustion on the fiber, salting out soaps, electrolyte addition in developing baths for 2-phase printing (prevents bleeding), and addition to water baths in the dye-house laboratory to achieve a higher boiling point.

2.13 Scanning electron microscope

The scanning electron microscope (SEM) is a microscope that uses electrons instead of light to form an image [26]. The scanning electron microscope is also known for using a beam of high-energy electrons producing variety of signals at the surface of solid specimens. These signals reveal the information about the sample including chemical composition, external morphology, crystalline structure and orientation of materials making up the sample [27]. Generally, the information is usually collected over a selected area of the surface of the sample and produces a 2-dimensional image that displays a difference in these properties. These areas are ranging from approximately 1 cm to 5 microns in width. The SEM has higher resolution for specimens with narrow space to be magnified at much higher levels. The degree of magnification is more controlled because the microscope uses electromagnets rather than lenses [26].
Magnification in a SEM can be controlled up to 6 orders of magnitude ranging from about 10 to 500,000 times.

2.13.1 Application

A beam of electrons is produced by an electron gun which is situated at the top of the microscope. The electron beam travels in a vertical path through the microscope, which is held within a vacuum. The beam is focused down toward the sample and once it hits the sample, electrons and X-rays are ejected from the sample [27]. The sample size must be able to fit in the specimen chamber and tightly placed on a specimen holder called a specimen stub. The sample(s) are coated with thin layer of conducting material, commonly carbon and gold which takes place by high vacuum evaporation.

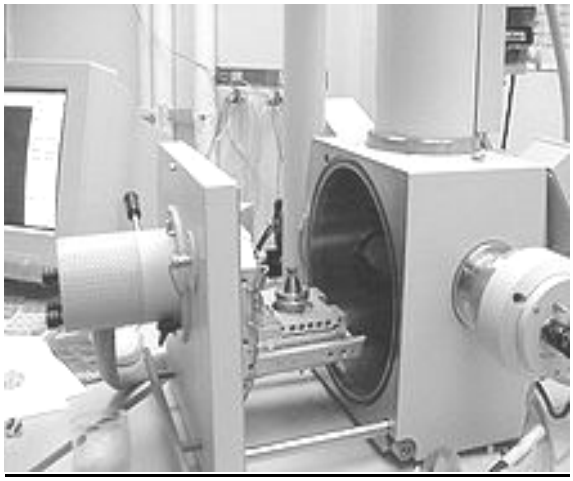


Figure 2.13: Schematic diagram of SEM

3. Experimental Part

3.1 Objectives of the experiment

1) Preparation of microparticles of model substances to verification of parameters and effectivity of spray dryer
2) Encapsulation of particles prepared by spray drying to fabric surface and observing of changes of properties
3) Preparation of capsules with PCM content, verification of its properties and application on textile.

3.2 List of chemicals

Sodium chloride-NaCl or commonly known as salt or ionic compound by Lach-Ner (Czech Republic)

Sodium carbonate- Na_2CO_3 or also known as soda ash. Alkaline

Gum Arabic - a natural gum also called **gum acacia**, is a substance that is taken from two sub-Saharan species of the acacia tree, Acacia senegal and Acacia seyal. Gum arabic is a complex mixture of saccharides and glycoproteins, which gives it one of its most useful properties and perfectly edible. It is used primarily as a stabilizer, oil-in-water emulsions; fixation of encapsulate flavor

Gelatine powder- an animal protein substance having gel-forming properties. Immersed in a liquid, gelatin takes up moisture and swells, causing the mixture to solidify. Gelatin melts to a liquid when heated and solidifies when cooled again. Together with water, it forms a semi-solid colloid gel. Gelatin forms a solution and emulsifier for gum Arabic.

Paraffin wax- heat storage material and applied as a phase change material

Acrylic binder-aqeuous dispersed co-polymer of butyl acrylate and styrene, they have good properties such as good heat stability, good solvent resistance, wet fastness and good fatsness test to dry cleaning.

Nonionic softener- esterified polyether dispersion, gives lubricating, certain moisture and absorbency to the fabric. This softener is easy to handle and resistant to yellowing. Suitable for cellulosic fibers and their blends with synthetic fibers for pad and exhaust process.

3.3 Preparation of microparticles

3.3.1 Preparation of sodium chloride using spray dryer

Material

Sodium chloride from company Lach-Ner (Czech Republic)

3.3.2 Spray drying method

Solution of sodium chloride was prepared in 250 ml volumetric flask. Sodium chloride was weighed in the laboratory scale and the concentration was place in the volumetric flask and mixed with 100 ml distilled water. The sodium chloride solution was spray-dried using a laboratory scale spray-drier (BÜCHI 290). The spray dryer parameters were set for the spray drying process. Solutions of sodium chloride were prepared in accordance to the settings of the spray dryer. Different setting of spray dryer parameters and concentrations of sodium chloride were used in determining the particle size of sodium chloride after spray drying process.

Laboratory scale spray-drier produced by BÜCHI Labortechnik AG, BÜCHI 290 was used for this study.

Figure 3.1: Laboratory scale spray-drier produced (BÜCHI 290)

3.3.3 Setting of spray dryer parameters

The experiment was divided into two parts, the first part which included sample 1, 2 and 3 were the aspiration and feed rate were kept constant while there was a difference in the inlet temperature. The second part includes sample 4, 5 and 6, the inspiration rate, inlet temperature and the feed rate were kept constant, while the concentration of sodium chloride had different values. All of the solutions were prepared in accordance to the settings of the spray dryer as shown in table 6. The samples were collected from the collecting container of the spray dryer and placed in a volumetric flask with a cover lid.
The samples (spray dried powder) were observed by using Scanning Electron Microscopy (Tescan digital microscopy imaging).

Table 6: Spray drying settings with different parameters

	Part 1			Part 2		
Samples	1	2	3	4	5	6
Concentration [g/l]	20	20	20	20	30	40
Inlet temperature [℃]	100	115	130	140	140	140
Aspiration rate [m^3/ min]	70	70	70	80	80	80
Feed rate [mL/min]	20	20	20	20	20	20
Actual inlet temperature [℃]	100	115	130	140	140	1 40
Outlet temperature [℃]	48	51	58	72	80	82

3.3.4 Preparation of sodium carbonate using spray dryer

The same procedure of spray drying sodium chloride was followed for preparation of sodium carbonate. Sodium carbonate solution was spray dried and the concentrations of sodium carbonate were mixed with distilled water. A volume of 100 ml for each sample was prepared for these solutions. The spray dryer parameters were set for the spray drying process. The solutions were atomized with a feed rate of 20 ml/min, and the first sample had an inlet and outlet temperature of 160 and 76 ^{O}C, respectively. The second sample had an inlet and outlet temperature of 180 and 82 ^{O}C, respectively and the third had temperatures of 200 and 91 ^{O}C. The aim of this procedure was observe the morphology of microcapsules by spray drying and the influences of drying temperature on the microcapsule sizes.

3.4 Application of sodium chloride on bicomponent fibers

3.4.1 Materials and Methods

Bicomponent (copolyester/polyester) fiber
Sodium chloride

Laboratory scale spray-drier (BÜCHI 290) was used for this study. The chosen fiber material for this experiment was a core/sheath type of bicomponent fiber. Polyester was the core and the copolyester was the sheath of the fiber. Diameters of both copolyester and polyester were measured to obtain their content in the fiber. The average diameter sizes of copolyester and polyester was 4.56 μm and 18.53 μm respectively. The bicomponent fiber had diameter size of 25.2μm. The application of sodium chloride on the fiber material is divided into two applications.

3.4.2 Application of sodium chloride directly on bicomponent by drying

3.4.2.1 First testing

The bicomponent fiber material was fixed to a metal wire and placed inside drying chamber, on the entrance of the tube which is situated between the drying chamber and cyclone. The metal wire was used to hold the fiber material not to move around the drying chamber. The concentration of sodium chloride was mixed with distilled water and prepared for spray drying process.
The solution was atomized with a feed rate of 5 ml/min, and the inlet and outlet temperature of 220 and 100 ^{O}C, respectively. The process of the droplets drying to solid particles takes place in the presence of the textile material. Not all particles are fixed unto the material, some passes through to the cyclone for separation of particles and falls down to the collection chamber. The dried solution was then collected from the container for further analysis. The fiber samples were observed through scanning electron microscopy for any changes in the fiber structure.

3.4.2.2 Second testing

The bi-component fibers were placed at the bottom of the collecting chamber of spray dryer for the micro particles to fall on the surface of the fibers. Similar process as in the first testing was followed but used different spray drying parameters. The weight of the fibers was 1.47 g for an evenly distributed powder on the material. The solution was atomized with a feed rate of 15 ml/min, and the inlet and outlet temperature of 140 and 80 ^{O}C, respectively. The fiber sample with the salt powder was collected for analysis. The fiber samples were observed through scanning electron microscopy for any changes in the fiber structure.

3.4.3 Application of sodium chloride on bi-component fibers by friction

3.4.3.1 Spray drying method

The concentrations of sodium chloride were mixed with distilled water. Two samples were prepared with same concentration (20 g/l) of sodium chloride. A volume of 100 ml for each sample was prepared for these solutions. Spray drying took place with setting of spray dryer parameters which were set according to table 7.

The samples were collected after the spray drying process for application on the fibers. A total of 4 fiber samples were weighted using a laboratory analytical scale. The spray dried powder (NaCl) was also weighed with different weights with correspondence to the weighed fiber samples. The fiber samples were weighed 0.2 g each and were applied with dried powder which weighed 10 times less than the weight of the fibers, while the other fiber samples were applied with approximately the same weight as the fibers. The listing of the weight of the fiber sample and the dried powder are shown in table 8.

3.4.3.2 Application of spray dried sodium chloride

Four fiber samples were prepared for application because one sample (dry powder) was applied on two fiber samples, as the samples were used for different processes. The dried powder from the first testing as shown in table 7 was applied on the two fibers, while the other sample from the second testing was applied on the other fibers.

3.4.3.3 Drying of samples

The fiber samples were dried in the laboratory oven dryer. Two different temperatures were used for this application. The first testing of fibers was at temperature ranging from 130-140℃ for a period of 1-2 minutes. The second testing was at temperature of 230^{O}C. The samples were cooled for a period. Two fiber samples were used for both testing, one sample was placed and washed into a beaker filled with 50 ml of distilled water and after the powder dissolved in the fibers, then the sample was dried at room temperature. The other (second) sample was dried at room temperature without washing off with water.
The fiber samples were observed through scanning electron microscopy for any changes in the fiber structure.

Table 7: Spray drying settings-different temperatures

Parameters	Testing 1	Testing 2
Inlet temperature [℃]	180	200
Aspiration rate [m^3/ min]	80	80
Feed rate [mL/min]	15	15
Actual inlet temperature [℃]	180	200
Outlet temperature [℃]	88	96

Table 8: Weights of samples and products

Samples	Testing	Weight of dried powder % [w/w]	Method
1	1	10	Drying
2	2	10	Drying
3	1	1	Drying
4	2	1	Drying
5	1	10	Washing off with water
6	2	10	Washing off with water
7	1	1	Washing off with water
8	2	1	Washing off with water

3.5 Preparation of microencapsulated PCM

3.5.1 Materials and Methods

Gum Arabic
Gelatin powder
Paraffin Wax

Testing I

Gum Arabic was weighed using a laboratory scale and mixed with water to make a gum solution. Gelatin powder was also weighed and mixed with distilled water to make a gelatin solution. Both of these solutions were mixed with an ultrasound homogenizer (fig 3.2) with a frequency of 20% and for a period of 4 minutes.

Gelatin and gum were weighed with the same ratio and paraffin wax with a different ratio, gelatin and gum Arabic was prepared as wall material and paraffin wax as a core material. This was prepared in different volume baths as shown in table 9. Paraffin wax had a melting temperature ranging from 52-54^{O}C. Gelatin solution was mixed with melted paraffin wax to form an emulsion. Emulsion of paraffin and gelatin was took place using the homogenizer. The gum solution was added to the emulsion of paraffin and gelatin, distilled water was added.

The emulsion of paraffin wax with gelatin-gum solutions were emulsified with an ultrasound homogenizer for 4 minutes with a frequency of 40%.The emulsion of paraffin wax with gelatin and gum solution was cooled at room temperature and prepared for the spray drying process.

Table 9: Preparation of phase change material

Sample	1	2	3	4
Gelatin powder [g]	0.5	0.5	0.5	0.25
Gum Arabic [g]	0.5	0.5	0.5	0.25
Paraffin wax [g]	0.5	1.0	0.5	0.5
Total volume [ml]	100	150	150	100

Testing II

The second process of preparing phase change material was using different melting temperatures of paraffin wax. The purpose of this procedure was to determine the difference in the behavior of the material and the morphological structure of the particle sizes.

Three samples were prepared using the same procedure as in testing I for emulsion process, with paraffin waxes of different melting temperatures was used.

The waxes were as follows, sample 5 (42-44^{O}C), sample 6 (50-52^{O}C) and sample 7 (58-60^{O}C), all these samples had the same weight of 2 grams. The samples were mixed with gelatin and gum weighing 1 gram each, and mixed with distilled water to make a volume of 100 ml.

The emulsion of paraffin wax with gelatin-gum solutions were emulsified with an ultrasound homogenizer for 4 minutes with a frequency of 40%.The emulsion of paraffin wax with gelatin and gum solution was cooled at room temperature and prepared for the spray drying process.

The emulsions from all samples both from testing I and II were atomized with a feed rate of 20 ml/min, and the inlet and outlet temperature of 130 and 80 ^{O}C, respectively. The dried samples were collected from the collecting chamber and placed in a container for analysis through DSC (Differential scanning colorimetry) for measuring the thermal storage of energy and the scanning electron microscope for the morphology of the material

Figure 3.2: Ultrasound homogenizer

4. Analytical Part

4.1 Preparation of sodium chloride using spray dryer

The samples collected from spray dryer were observed by using Scanning Electron Microscopy (Tescan digital microscopy imaging) as shown in figure 4.1a.

Figure 4.1a: Scanning Electron Microscopy **Figure 4.1b**: Ion sputter

The prepared samples were placed on the metallic-end with a double-coated adhesive tape. The samples were coated with a thin layer of sputtered gold prior to examination, using an ion sputter JEOL JFC 1100 device as shown in figure 4.1b. The samples were placed in the vacuum of the microscopy for analysis. Three different types of magnifications were used for analysis, the magnitude were as follows (5, 7 and 10 x). The images were taken from the microscopy and collected for measurements of particle sizes. Each sample had different image analysis, for instance three to five images were taken from one sample. The particle sizes were measured using LUCIA G software analysis.

4.2 Measurements of sodium chloride particles

The images from scanning electron microscopy were collected for analysis. The particle sizes from the images were measured using LUCIA G software analysis. The diameter of particle size was measured from each image with a minimum of 30 measurements.
Three samples were analyzed and from each sample, two measurements were analyzed for comparing any variation between the images. Three testing were conducted with each testing containing three samples. The first part of testing was measuring the particles sizes of three different samples that were spray dried with different inlet temperatures. The second part of testing included measurement of sample with different feed rates, and the third testing was with different solid concentrations. All of these testing's and parameters are described in table 10. These measurements were analyzed and statistical parameters such as minimum, maximum and mean value were obtained as shown in table 10.1, 10.2 and 10.3.

4.3 Application of spray dried powder on bicomponent fibers

The prepared fiber samples that were applied with spray dried sodium chloride were collected for analysis through the scanning electron microscope. Optical images were taken from these samples. The structures of the fiber sample were observed for any changes in the fiber structure.

4.4 Measurements of phase change material

The samples were collected from the encapsulated phase change material for analysis through scanning electron microscopy. Magnification of 5.00 x was used for this analysis with a size of 10 µm. Images were taken from all seven samples of the encapsulated product. These images were used for measuring the diameter of the microcapsules sizes using LUCIA G software analysis. A maximum of 30 measurements were taken for measuring the diameter of the capsules. The capsule sizes were obtained with diameters ranging from minimum to maximum values, the average value and standard deviation of the capsule were determined through the software as shown in table 11.

5. Results and discussion

5.1 Characterization of microparticles

5.1.1 Measurements of particle size of sodium chloride

First part of testing of particle sizes

The purpose of this testing was to measure if the inlet temperature has an influence in the particle sizes. Three different inlet temperatures were chosen for this testing and particle sizes were measured for each sample as shown in table 10.1. For the first sample, the particle sizes were ranging from [1-4.56 µm] with an average value of 2.51 µm and a standard deviation of 0.93. The particle sizes of second sample were ranging from [1.28-5.78 µm] with an average value of 2.63 µm and a standard deviation of 1.08. The third sample had particle sizes ranging from [0.96-4.36 µm] with an average value of 2.41 µm and a standard deviation of 0.70. The average values for each sample shows small variance between samples. This shows that when the inlet temperature increases, the particle sizes increase variably which has no significant difference among the samples. Thus, the temperature has no influence on the particle sizes of the sample.

Second part of testing of particle sizes

The second part of testing measured the influence of solid concentration on the particle size. Samples were prepared with three different concentrations. These samples were measured with comparison of the particle size as shown in table 10.2.
The first sample (sample 5) was measured with particle sizes ranging from [0.46-1.43 µm] with an average value of 0.95 µm and a standard deviation of 0.26. The particle sizes of second sample were ranging from [0.52-4.05 µm] with an average value of 1.30 µm and a standard deviation of 0.66. The third sample had particle sizes ranging from [0.96-4.36 µm] with an average value of 1.95 µm and a standard deviation of 0.78. There more solid concentration in the solution, the bigger the particles. The solid concentration in the solution has an influence on the particle size of the sample.

Table 10.1: Measurements of the first part of testing of particle sizes

Sample	Sample 1	Sample 2	Sample 3
Items	Length (µm)	Length (µm)	Length (µm)
1	3.358	2.21	2.436
2	4.558	2.123	1.286
3	2.434	1.427	1.900
4	1.955	3.662	2.869
5	3.252	5.776	2.618
6	4.052	5.196	4.084
7	4.293	2.174	3.484
8	2.778	3.839	2.670
9	2.783	1.427	2.905
10	2.751	1.285	2.682
11	3.029	1.608	3.455
12	1.276	3.008	1.073
13	1.725	3.694	2.805
14	1.809	2.262	2.094
15	1.877	3.039	2.498
16	1.677	1.345	2.466
17	1.364	1.874	2.616
18	2.293	1.65	2.011
19	2.317	2.769	2.927
20	2.024	2.42	2.948
21	3.239	1.929	0.951
22	3.409	1.926	3.131
23	3.631	3.43	2.349
24	1.005	1.859	1.864
25	1.067	2.386	2.282
26	2.158	2.529	1.398
27	2.06	3.305	1.826
28	3.223	2.866	2.247
29	2.199	2.682	1.837
30	1.677	3.141	2.501
Minimum [µm]	1	1.28	0.95
Maximum [µm]	4.56	5.78	4.08
Mean [µm]	2.51	2.63	2.41
Standard deviation	0.93	1.08	0.7

Table 10.2: Measurements of the second part of testing of particle sizes

Sample	Sample 4	Sample 5	Sample 6
Items	Length (µm)	Length (µm)	Length (µm)
1	0.984	2.347	2.439
2	0.787	1.948	1.462
3	0.904	0.831	1.677
4	0.628	0.964	4.357
5	1.186	0.787	4.116
6	1.143	0.309	3.039
7	1.126	1.423	2.563
8	1.310	2.838	1.285
9	0.860	1.495	2.204
10	1.025	1.267	2.673
11	1.223	3.370	1.286
12	1.144	1.864	1.733
13	0.878	2.090	1.680
14	0.905	0.904	1.782
15	0.580	0.785	1.598
16	1.010	1.203	1.740
17	0.576	0.821	1.152
18	0.976	0.878	2.018
19	0.935	1.239	2.234
20	1.000	0.966	1.534
21	1.069	1.145	1.926
22	1.146	0.762	1.479
23	1.431	0.875	1.476
24	1.340	0.703	2.453
25	0.860	0.514	1.643
26	1.362	0.387	1.085
27	0.564	0.710	2.087
28	0.455	3.357	0.956
29	0.488	0.647	1.703
30	0.707	1.084	1.229
Minimum [µm]	0.46	0.31	0.96
Maximum [µm]	1.43	3.37	4.36
Mean [µm]	0.95	1.28	1.95
Standard deviation	0.26	0.8	0.78

5.1.2 Structure of the microparticles

The optical microphotographs were taken after spray drying of sodium chloride. From the first part of testing of spray dried sodium chloride, the particles from the first sample showed small particle sizes with square shapes. Some of these particles combined together and formed round structures. The distributions of the particle sizes were uniform with different sizes as shown in figure 5.1a.
The second sample, because of different temperature from the first sample, the particles appeared to be uniform with more or less the same sizes and showed narrow distribution amongst the particles as shown in figure 5.1b.
The third sample had a high quantity of small particles and less of big particles. The particles were closely packed to each other as shown in figure 5.2a.

The second part of testing of spray drying was using different concentrations of sodium chloride. The first sample showed different shapes and sizes of particles, most particles were small compared to the big particles. Most particles were combined together with round shapes as shown in figure 5.2b.
The particles from the second sample appeared to be larger compared to the first sample. The particles formed blocks which were close to each other and the distribution was uneven as there were spaces between some of the particles as shown in figure 5.3a.
The third sample showed particles of larger sizes with blocks of rounded shapes. There were more spaces in between the particles as shown in figure 5.3b.

Sample 1	Sample 2

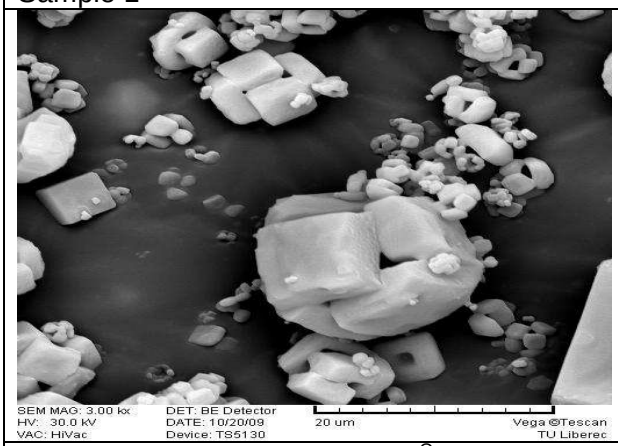
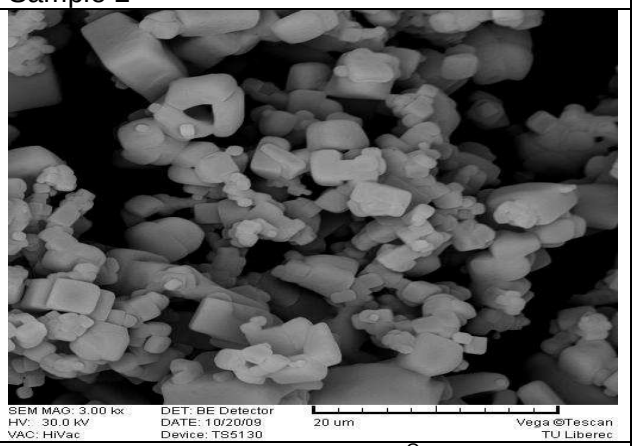

	

Figure 5.1a: Spray drying T-100^{O}C (20 g/l NaCl), particles with magnification of 3.00 x, scale bar = 20 µm	Figure 5.1b: Spray drying T-115^{O}C (20 g/l NaCl), particles with magnification of 3.00 x, scale bar = 20 µm

Sample 3	Sample 4

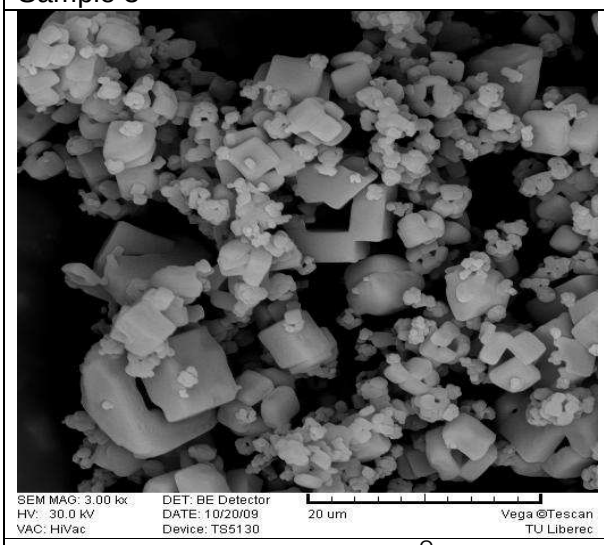
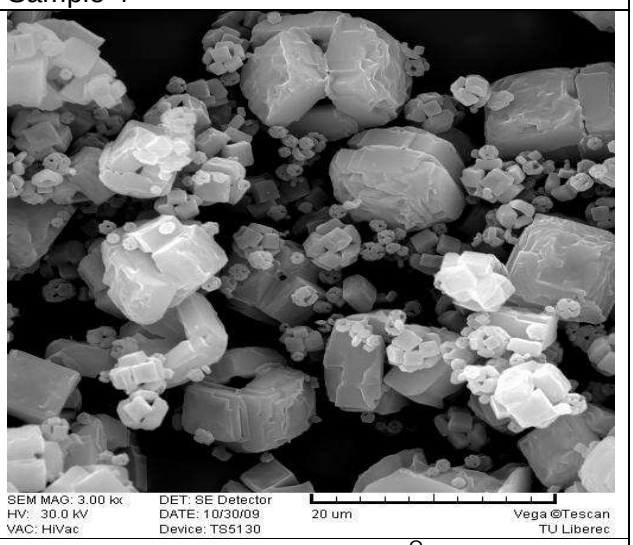

	

Figure 5.2a: Spray drying T-130^{O}C (20 g/l NaCl), particles with magnification of 3.00 x, scale bar = 20 µm	Figure 5.2b: Spray drying T-140^{O} C (20 g/l NaCl), particles with magnification of 3.00 x, scale bar = 20 µm

Sample 5	Sample 6

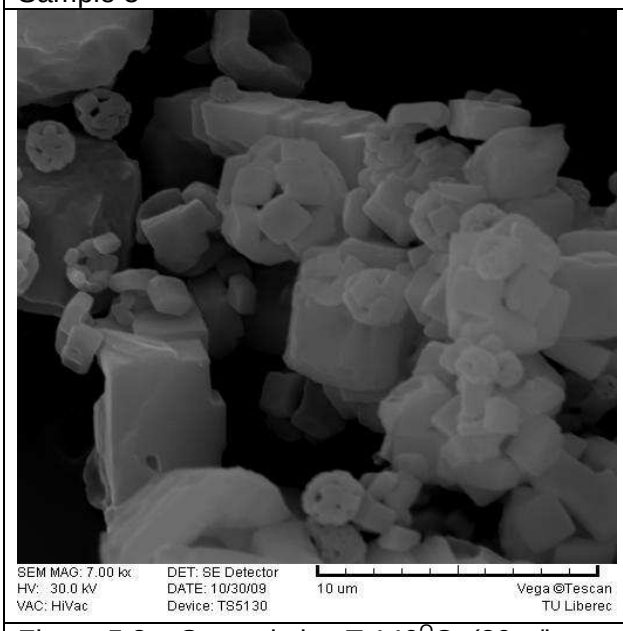
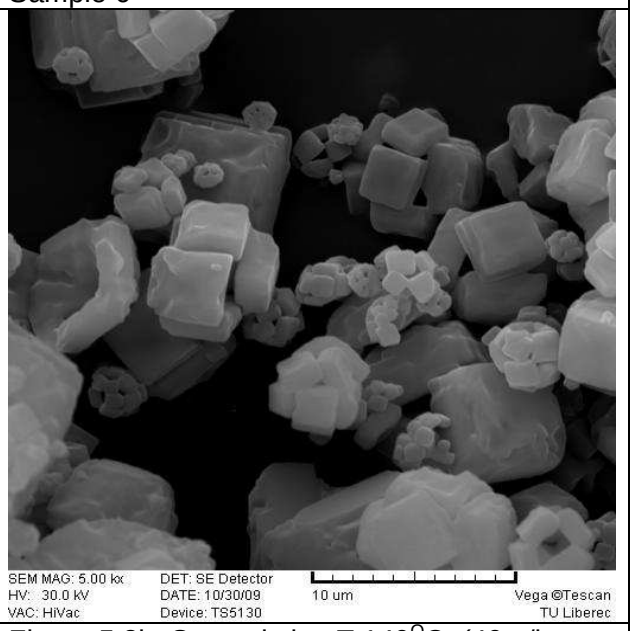

	

Figure 5.3a: Spray drying T-140^{O}C, (30 g/l NaCl),, particles with magnification of 7.00 x, scale bar = 10 µm	Figure 5.3b: Spray drying T-140^{O}C, (40 g/l NaCl),, particles with magnification of 5.00 x, scale bar = 10 µm

5.1.3 Application of spray dried powder on bicomponent fibers

First application

The first application of spray dried powder on bicomponent fibers was by applying friction between the powder and the fiber samples. After application of powder on samples, sample 1 and 2 was dried at a temperature of 90^{O}C. Through the micrographs that were taken from microscope, the two samples showed a change in the outer structure of the fibers. The first and second sample appeared to have rough surfaces on the fiber structure as shown in figure 5.4a and 5.4b.

The images of sample 3 and 4 showed cracks and rough surfaces on the fiber structure. Traces of small particles were also observed on the fiber surface. Comparing with the first samples, the fiber samples were applied with small quantity of powder than in the second samples. That is why the second sample has small particles on the surface of the fiber as shown in figure 5.5a and 5.5b.

Sample 1	Sample 2

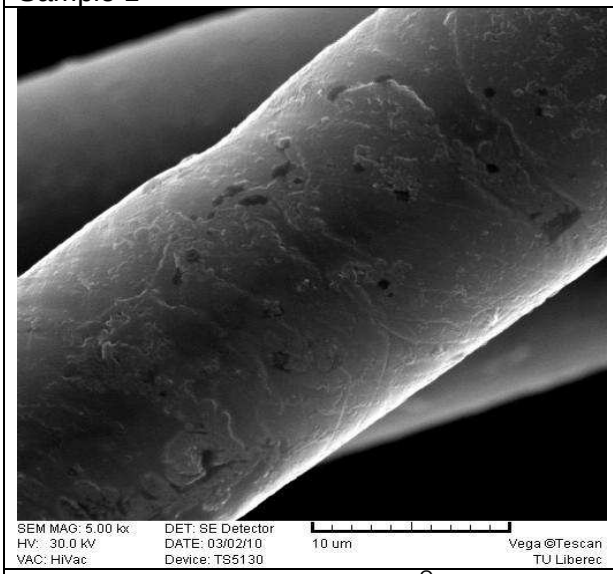
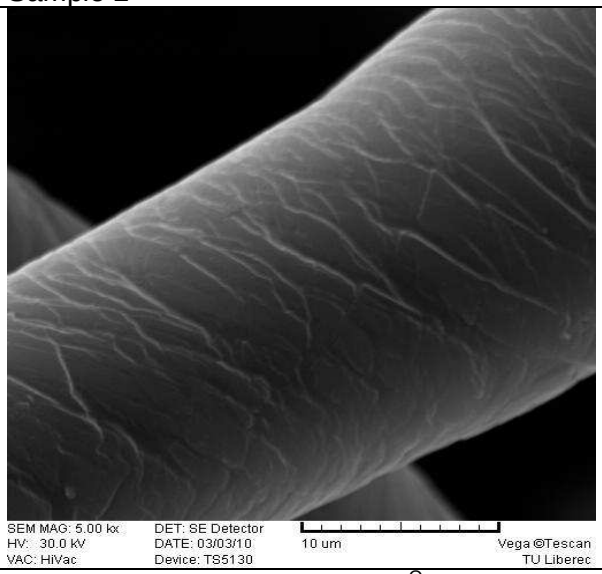

	

Figure 5.4a: Spray drying T-180^{O}C with small amount of powder, images with magnification of 5.00 x, scale bar = 10 µm	Figure 5.4b: Spray drying T-200^{O}C with small amount of powder, images with magnification of 5.00 x, scale bar = 10 µm

Sample 3	Sample 4

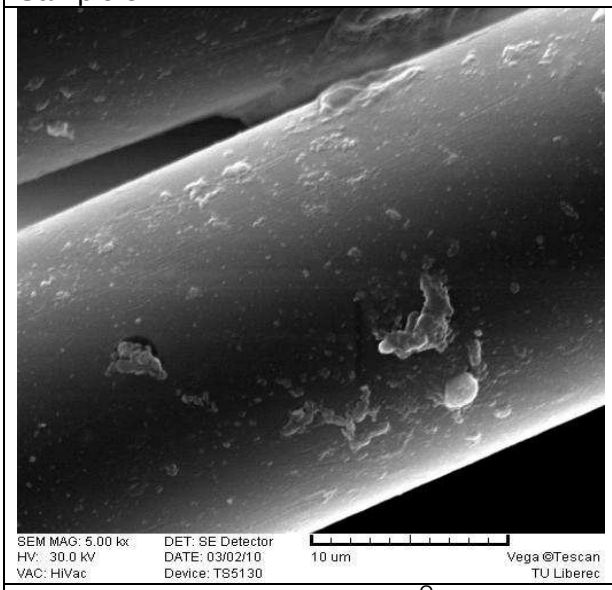
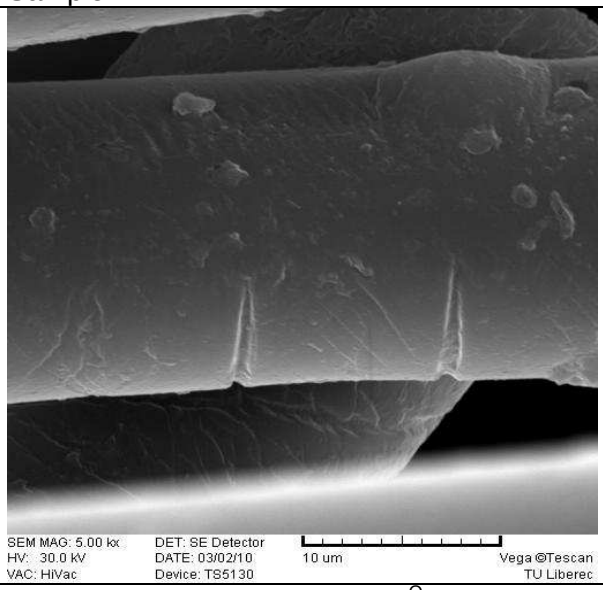

	

Figure 5.5a: Spray drying T-180^{O}C with high amount of powder, images with magnification of 5.00 x, scale bar = 10 µm	Figure 5.5b: Spray drying T-200^{O}C with high amount of powder, images with magnification of 5.00 x, scale bar = 10 µm

The four samples (5, 6, 7 & 8) were prepared by application of spray dried powder on fibers samples and were washed with distilled water.

Sample 5 showed rough surface on fiber structure and traces of small particles on the fiber surface as shown in figure 5.6a. Sample 6 appeared to have holes on the fiber surface where the small particles destroyed the surface and stuck inside the fiber, and other small particles were observed on the fiber surface as shown in figure 5.6b.

Sample 7 showed rough surface with small particles attached to the fiber structure and some particles stuck on the fiber surface as shown in figure 5.7a. Sample 8 also showed traces on particles stuck on the fiber surface with rough structure as shown in figure 5.7b.

Sample 5	Sample 6

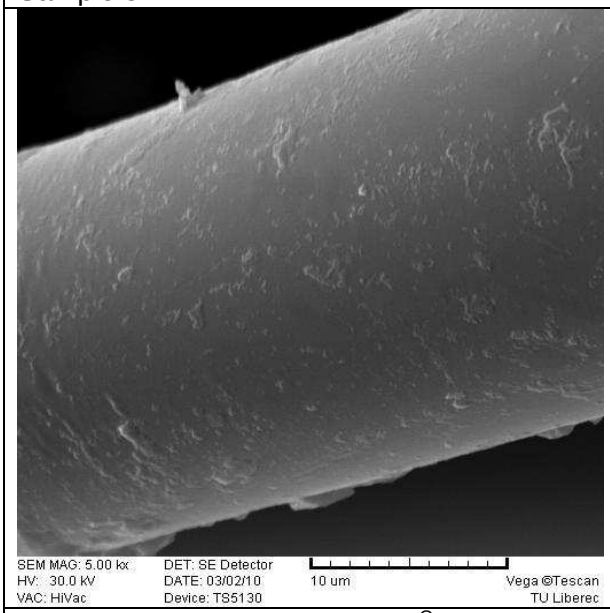
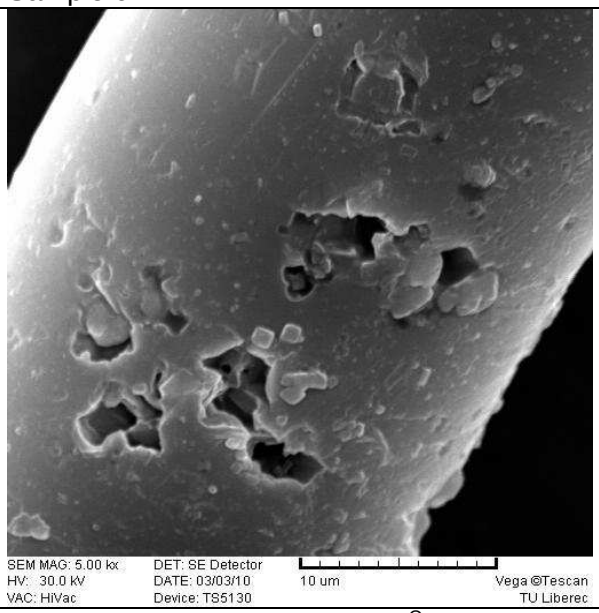

	

Figure 5.6a: Spray drying T-180^{O}C with small amount of powder, images with magnification of 5.00 x, scale bar = 10 µm	Figure 5.6b: Spray drying T-200^{O}C with small amount of powder, images with magnification of 5.00 x, scale bar = 10 µm

Sample 7	Sample 8

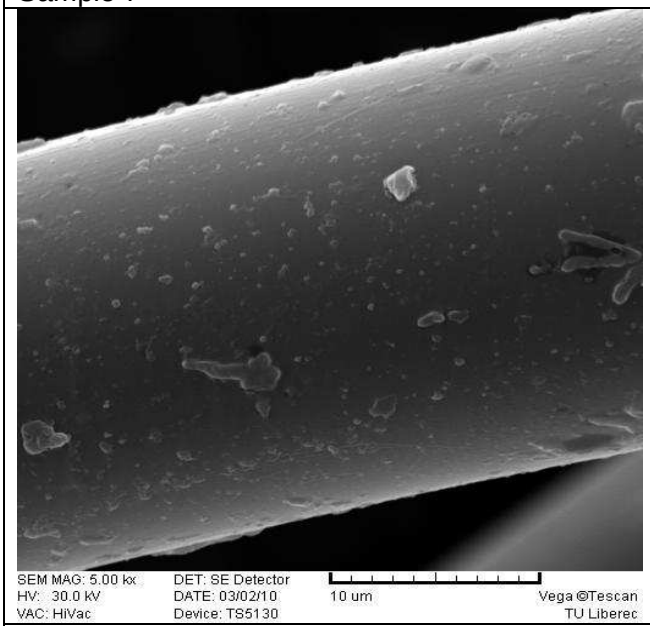
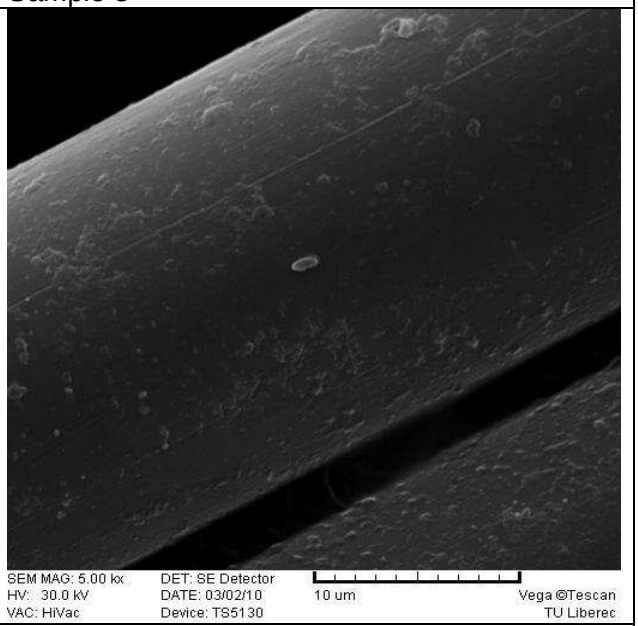

	

Figure 5.7a: Spray drying T-180^{O}C with high amount of powder, images with magnification of 5.00 x, scale bar = 10 µm	Figure 5.7b: Spray drying T-200^{O}C with high amount of powder, images with magnification of 5.00 x, scale bar = 10 µm

5.1.4 Application of sodium chloride directly on bicomponent fibers by drying

5.1.4.1 First part of testing

The first part of testing was by placing the bicomponent fiber inside the drying chamber. After application of spray dried powder on the fiber samples, the sample were collected and dried. From the microscopic images, sample 1 appeared to have holes on the fiber structure. The fiber surface had holes with particles attached inside the holes and others were attached on the surface of the fiber as shown in figure 5.8a.
Sample 2 had rough surfaces and most of the fiber surface was destroyed. The fiber had cracks and openings which were attached to each other forming big openings on the fiber surface. Sample 2 had less of particle on the fiber surface compared to the first sample; this is due to the process of washing off the sample with distilled water as shown in figure 5.8b.
Sample 3 also showed traces of particles inside opening on the fiber surface, small openings were observed on the fiber as shown in figure 5.9a.
Sample 4 showed small particles on the surface of the fiber and fractured surface as shown in figure 5.9b. Sample 4 had small traces of particles compared to the third sample. Both sample 3 and 4 were applied with particles which were prepared with a different inlet temperature of spray drying, which was different from sample 1 and 2. Fiber surfaces of sample 1 and 2 were more damaged than sample 3 and 4. The samples that were washed with water had less traces of particle and more openings or damages on the fiber surface.

Sample 1	Sample 2

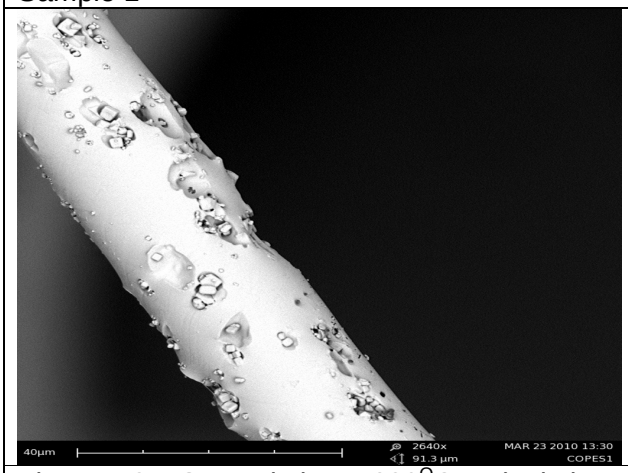
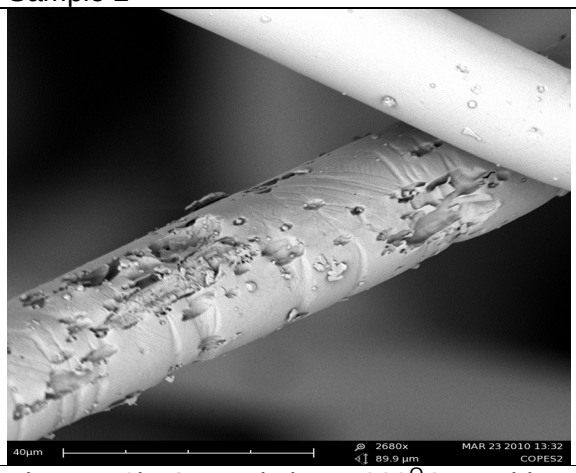

	

Figure 5.8a: Spray drying T-220^{O}C, only drying, images with magnification of 2640 x, scale bar = 40 µm	Figure 5.8b: Spray drying T-220^{O}C, washing of samples, images with magnification of 2680 x, scale bar = 40 µm

Sample 3	Sample 4

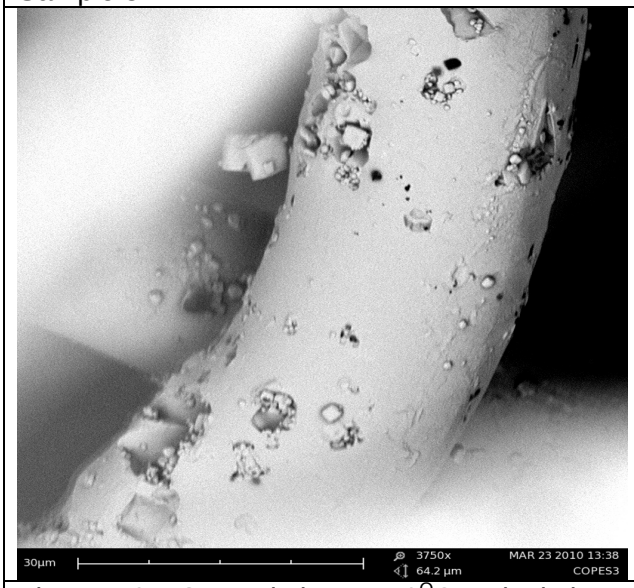
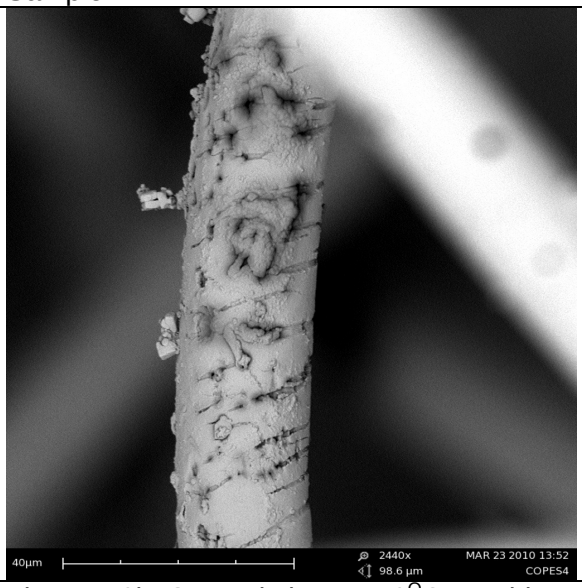

	

Figure 5.9a: Spray drying T-140^{O}C, only drying, images with magnification of 3750 x, scale bar = 30 µm	Figure 5.9b: Spray drying T-140^{O}C, washing of samples, images with magnification of 2440 x, scale bar = 40 µm

5.1.4.2 Second part of testing

The second part of testing was following the same procedure as in the first part of testing, where the sample were collected and dried near the melting temperature of the fibers for dissolving of particles. The fiber samples were collected for image analysis, the micrographs showed outer structure of the fiber samples.

Sample 1 appeared to have lots of particles on the surface of fiber as shown in figure 5.10a and sample 2 had no particles but had fractured surface and openings on the fiber structure as shown in figure 5.10b. Sample 3 showed particles which were on top of the surface and sample 4 appeared to have particles fixed inside the fiber structure as shown in figure 5.11a and 5.11b respectively. Sample 2 and 4 has fewer traces of particles as compared to sample 1 and 3, because it was washed off with water. These samples showed less damage of fiber structure compared to the samples that were dried with lower temperature.

Sample 1	Sample 2

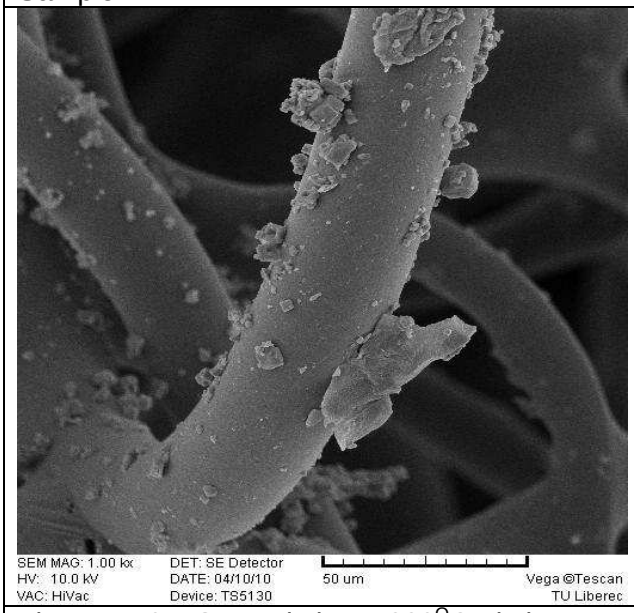
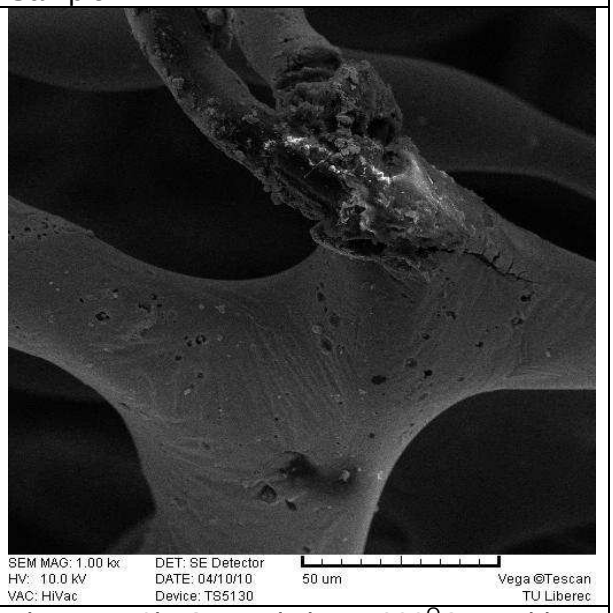

	

Figure 5.10a: Spray drying T-220^{O}C, drying samples at temperature of 230^{O}C, images with magnification of 1.00 x, scale bar = 50 µm	Figure 5.10b: Spray drying T-220^{O}C, washing of samples, images with magnification of 1.00 x, scale bar = 50 µm

Sample 3	Sample 4

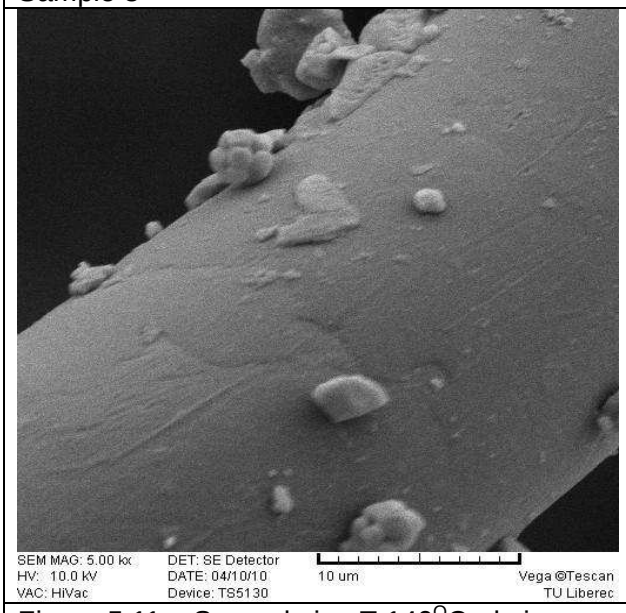
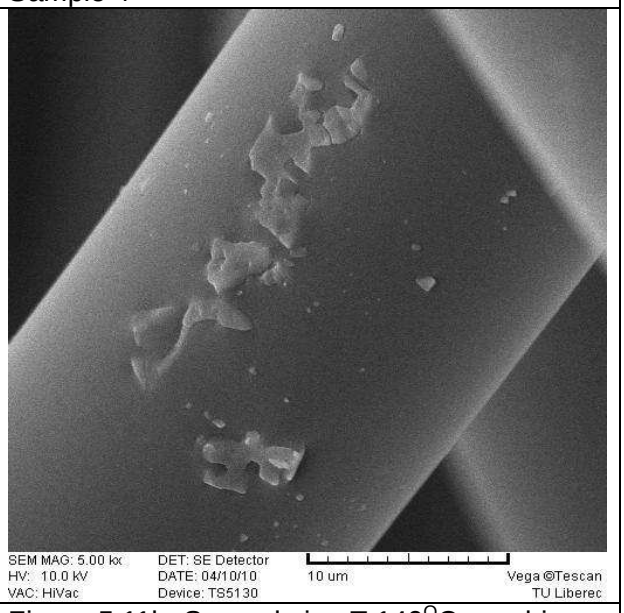

	

Figure 5.11a: Spray drying T-140^{O}C, drying samples at temperature of 230^{O}C, images with magnification of 5.00 x, scale bar = 10 µm	Figure 5.11b: Spray drying T-140^{O}C, washing of samples, images with magnification of 5.00 x, scale bar = 10 µm

5.2 Characterization of microcapsules

5.2.1 First part of measuring diameter of PCM microcapsules

Through the preparation of phase change material, gelatin and gum Arabic was prepared as wall material and paraffin wax as a core material. Encapsulation of phase change material was prepared in terms of ratio between the wall and core material. The first testing was carried out by using the same melting temperature but using ratio between the wall and core material and different volumes of bath as shown in table 11.1.

Sample 1 and 3 had the same ratio (1:1) of wall and core material, prepared in different baths with 100 and 150 ml respectively. The higher quantity of water increases the mean diameter from 1.64 to 2.25 µm and the standard deviation from 0.54 to 1.55. The more water is added in the bath the higher the mean diameter of the capsules.

Sample 2 and 3 had a ratio of 1:2 (wall: core) and 1:1 prepared in different baths with the same volume. These baths contained different quantity of paraffin wax with one bath having twice the quantity than the other. Reduction of the quantity of wax increases the mean diameter from 1.77 to 2.55 µm and the standard deviation from 0.66 to 1.55. It is observed that using a high quantity of wax results in small mean diameter of capsules.

Sample 1 and 4 with ratios 1:1 and 1:2 respectively were prepared in different baths with the same volume. The difference was one bath had a smaller quantity of gum and gelatin (wall material) than the other. Reduction of the quantity of wall material increases the mean diameter from 1.64 to 1.76 µm and the standard deviation from 0.54 to 0.60. Smaller quantity of wall material results in a higher mean diameter. An addition or increase in quantity of paraffin wax and gelatin-gum increases the microcapsule mean diameter.

5.2.2 Second part of measuring diameter of PCM microcapsules

The second part of testing was carried out using paraffin waxes with different melting temperatures. This testing was measured to determine the influence of different melting temperatures of paraffin wax to the diameter of the microcapsules. The microcapsule sizes for all three samples were ranging from 0.7 to 5 µm with standard deviation ranging from 0.60 to 1. The mean diameter of the samples was ranging from 1.7 to 2.22 µm. Thus, the usage of paraffin waxes with different melting temperatures under the same conditions has little influence on the mean diameter of the microcapsules.

Table 11.1: Measurements of first testing of PCM microcapsules diameter

Sample	Sample 1	Sample 2	Sample 3	Sample 4
Items	Length (µm)	Length (µm)	Length (µm)	Length (µm)
1	2.145	2.352	4.811	2.704
2	1.582	2.347	2.197	1.931
3	2.065	1.657	3.459	0.826
4	1.633	1.835	0.860	1.433
5	1.273	1.320	1.223	1.405
6	2.86	1.853	1.397	1.784
7	2.506	2.381	2.477	2.646
8	2.446	1.323	1.41	2.303
9	0.621	1.027	1.176	2.749
10	1.700	1.214	1.67	2.339
11	1.346	1.450	2.603	1.757
12	1.786	1.069	1.209	1.172
13	1.408	2.997	8.078	2.800
14	1.294	1.763	3.299	2.186
15	1.010	1.941	3.356	1.576
16	1.457	0.792	5.205	2.632
17	2.238	2.206	2.555	1.629
18	1.218	1.595	1.469	1.554
19	1.591	1.559	1.155	0.822
20	1.455	0.990	2.917	1.453
21	1.276	2.625	1.829	1.829
22	1.605	1.140	2.714	1.792
23	1.366	2.120	1.242	1.362
24	1.010	2.305	2.131	1.172
25	1.040	3.552	1.641	1.792
26	1.699	1.857	1.267	2.306
27	1.596	1.164	1.138	1.942
28	1.809	0.841	1.393	0.912
29	3.023	1.143	0.931	1.083
30	1.267	0.971	0.572	0.858
Minimum [µm]	0.62	0.79	0.57	0.82
Maximum [µm]	3.02	3.55	8.08	2.8
Mean [µm]	1.04	1.77	2.25	1.76
Standard deviation	0.54	0.66	1.55	0.6

Table11.2: Measurements of second testing of PCM microcapsules diameter

Sample	Sample 5	Sample 6	Sample 7
Items	Length (µm)	Length (µm)	Length (µm)
1	2.429	2.063	1.767
2	2.192	1.171	2.145
3	1.552	1.725	2.205
4	1.221	1.605	1.616
5	1.460	2.118	2.147
6	3.674	0.800	4.060
7	2.468	1.591	3.233
8	4.998	1.655	2.843
9	2.475	1.718	3.437
10	1.740	1.866	1.992
11	1.216	0.926	1.545
12	0.739	3.519	1.895
13	1.352	2.405	2.616
14	0.878	1.461	2.277
15	1.083	4.464	1.694
16	1.125	3.269	3.212
17	1.651	1.393	3.671
18	1.033	2.253	0.966
19	1.001	1.953	3.636
20	1.909	1.859	1.514
21	1.301	1.458	3.388
22	1.366	1.829	0.775
23	2.620	1.618	1.341
24	1.192	0.853	1.461
25	2.291	1.549	1.334
26	1.566	1.118	1.611
27	3.053	0.938	1.075
28	3.025	1.698	2.673
29	1.620	1.106	3.285
30	1.338	1.207	1.061
Minimum [µm]	0.74	0.8	0.78
Maximum [µm]	5.00	4.46	4.06
Mean [µm]	1.85	1.77	2.22
Standard deviation	0.92	0.79	0.91

5.2.3 The morphology of the microcapsules

The optical microphotographs were taken after spray drying, many small capsules were observed in images that were taken from the prepared samples. Most samples showed small particles with sizes ranging from 0.6 to 8 μm.

Sample 1 appears to have small microcapsules which are clustered and has uneven distribution of capsule sizes, most capsules have similar sizes with diameters ranging between 1 and 2 μm as shown in figure 5.12a.

Sample 2 has a wider distribution of capsules and most of the capsules are grouped and attached to each other. The capsule sizes are similar to the first sample as shown in figure 5.12b.

Sample 1	Sample 2

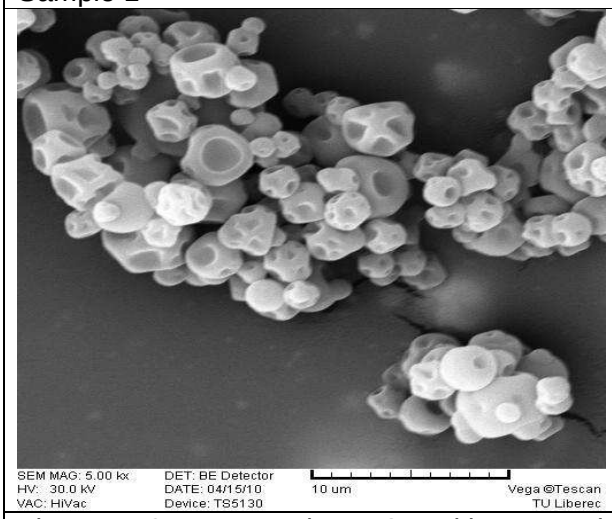
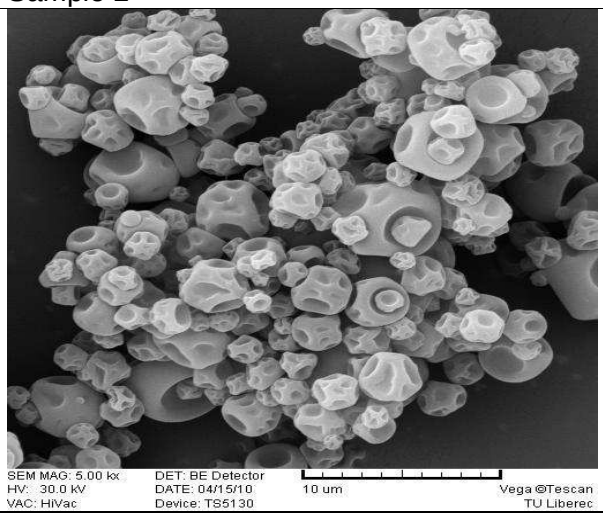

	

Figure 5.12a: Encapsulate PCM with core and wall material (1:1) and small volume of water, magnification of 5.00 x, scale bar = 10 μm	Figure 5.12b: Encapsulate PCM with core and wall material (1:2) and high volume of water, magnification of 5.00 x, scale bar = 10 μm

Sample 3 has an uneven distribution of capsules; capsules are attached together with a variety of big and small sizes. The sizes of capsules varied with diameters less than 2 μm as shown in figure 5.13a. Sample 4 showed different sizes of capsules with diameters less than 2 μm, most capsules were attached together with formation of blocks and there were spaces in between capsules as shown 5.13b.

Sample 3	Sample 4

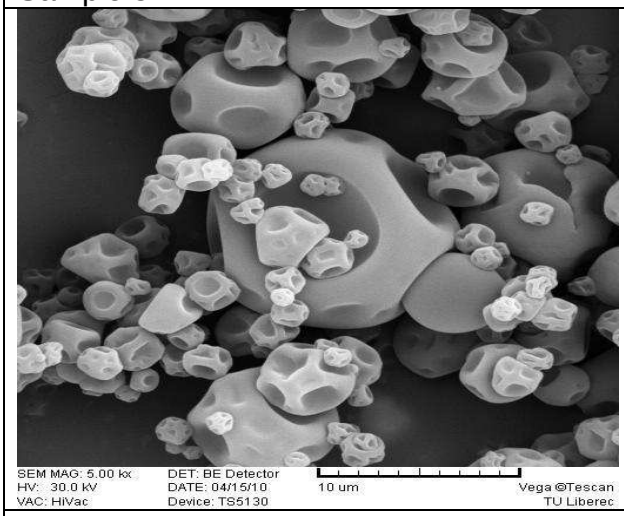
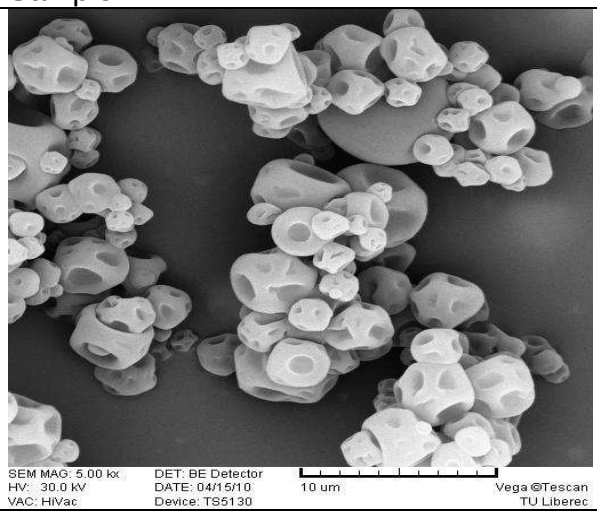

	

Figure 5.13a: Encapsulate PCM with core and wall material (1:1) and high volume of water, magnification of 5.00 x, scale bar = 10 µm	Figure 5.13b: Encapsulate PCM with core and wall material (1:2) and small volume of water, magnification of 5.00 x, scale bar = 10 µm

Sample 5	Sample 6

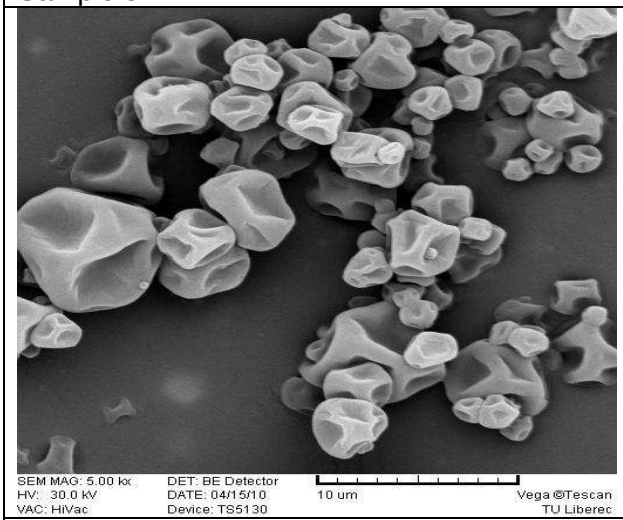
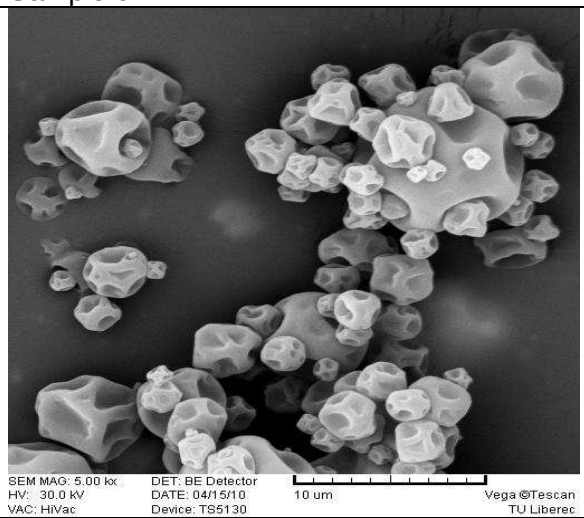
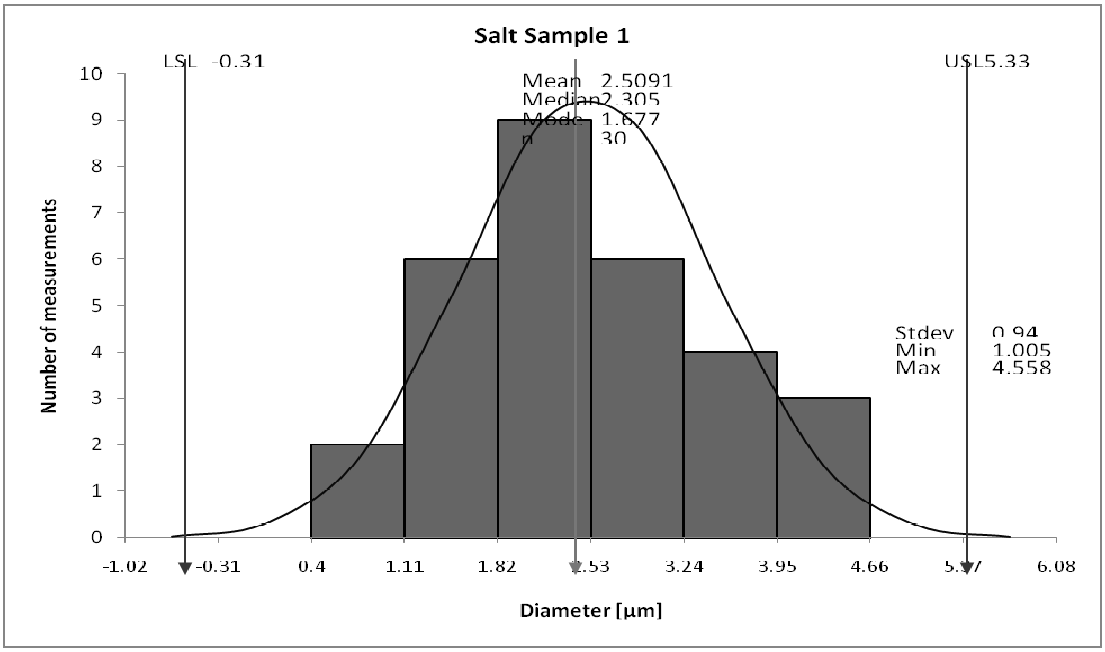

	

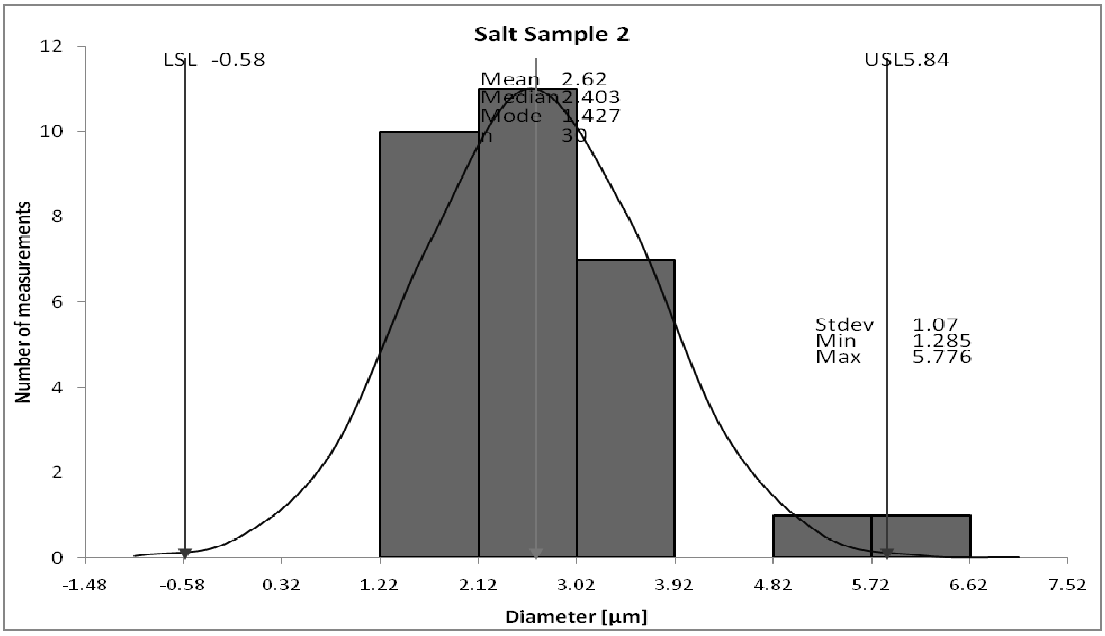
Figure 5.14a: Encapsulate PCM with core and wall material (2:1) with Tm-[42-44^{O}C], magnification of 5.00 x, scale bar = 10 µm	Figure 5.14b: Encapsulate PCM with core and wall material (2:1) with Tm-[50-52^{O}C], magnification of 5.00 x, scale bar = 10 µm

Sample 5 contains capsules with small sizes and most are attached together. The sizes of capsules varied with diameters less than 1.5 µm as shown in figure 5.14a. Sample 6 showed different sizes of capsules in which most had small sizes with diameters less than 2 µm, the capsules were attached together with formation of blocks and there were spaces in between capsules as shown 5.14b.

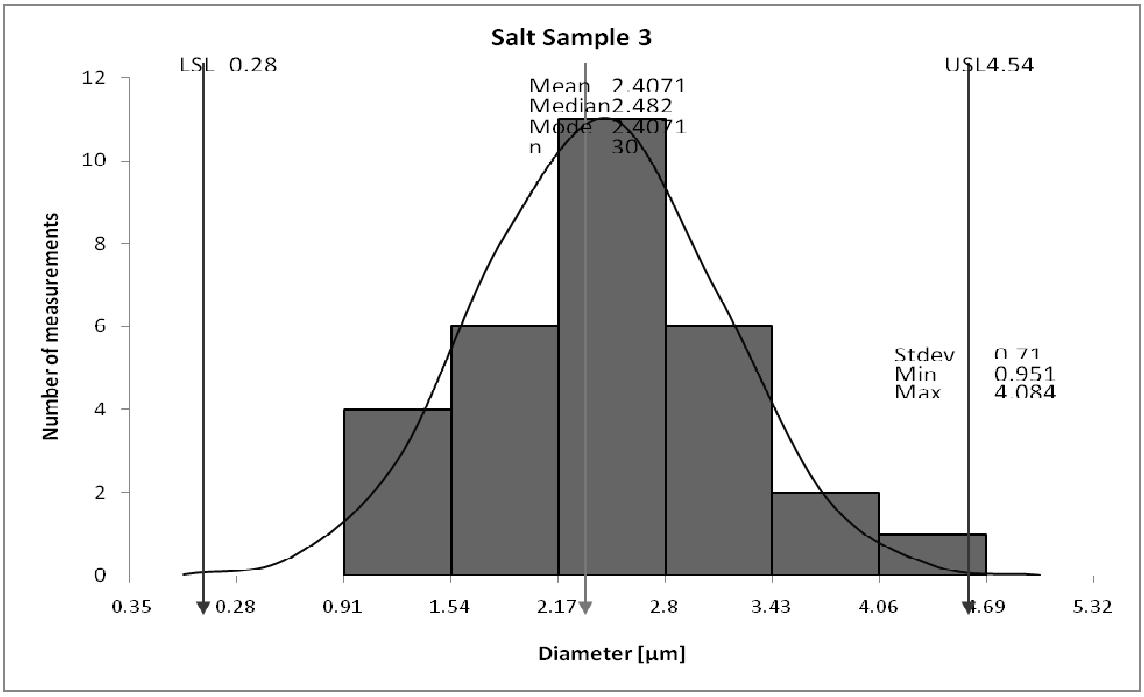
5.2.4 Graphs



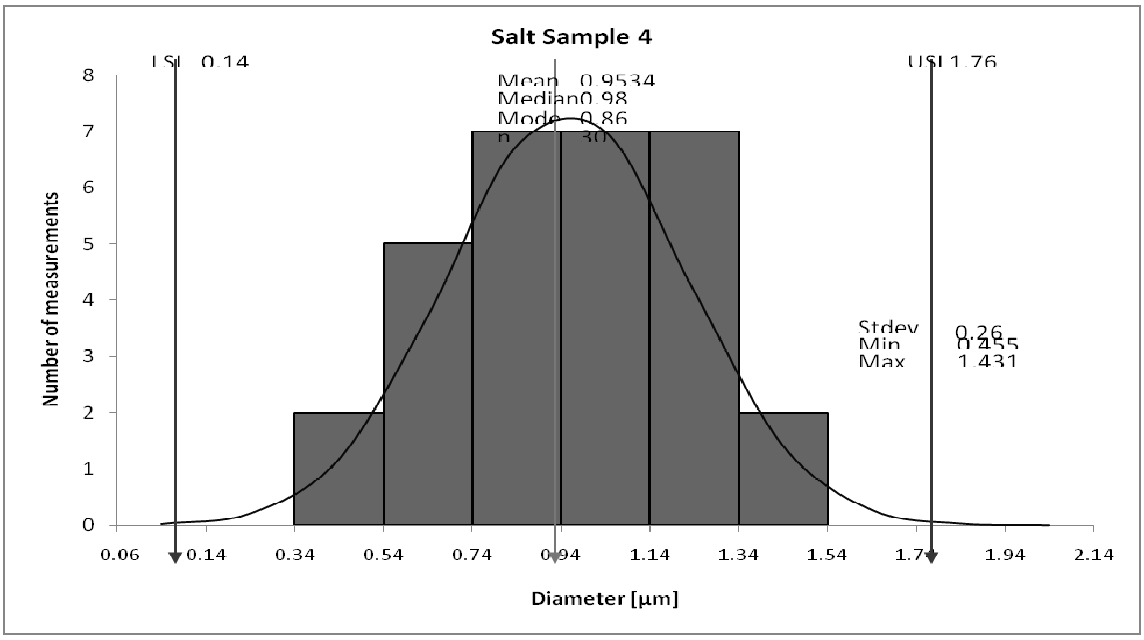
Graph 5.1: Sizes of particles of sample 1 of spray dried sodium chloride



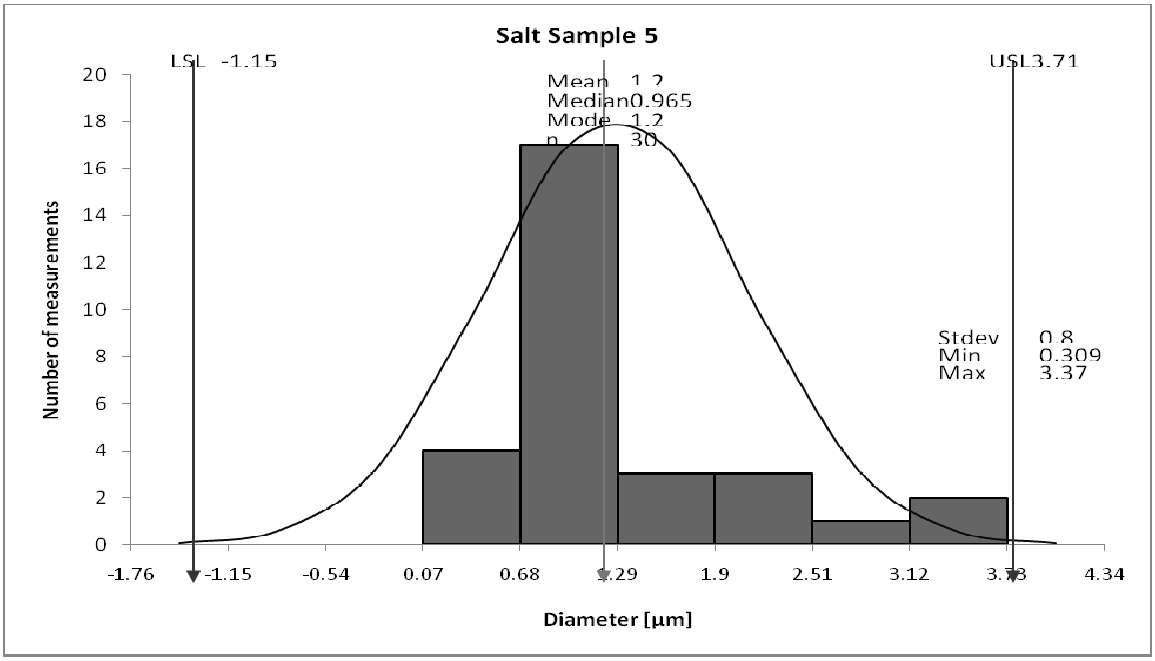
Graph 5.2: Sizes of particles of sample 2 of spray dried sodium chloride



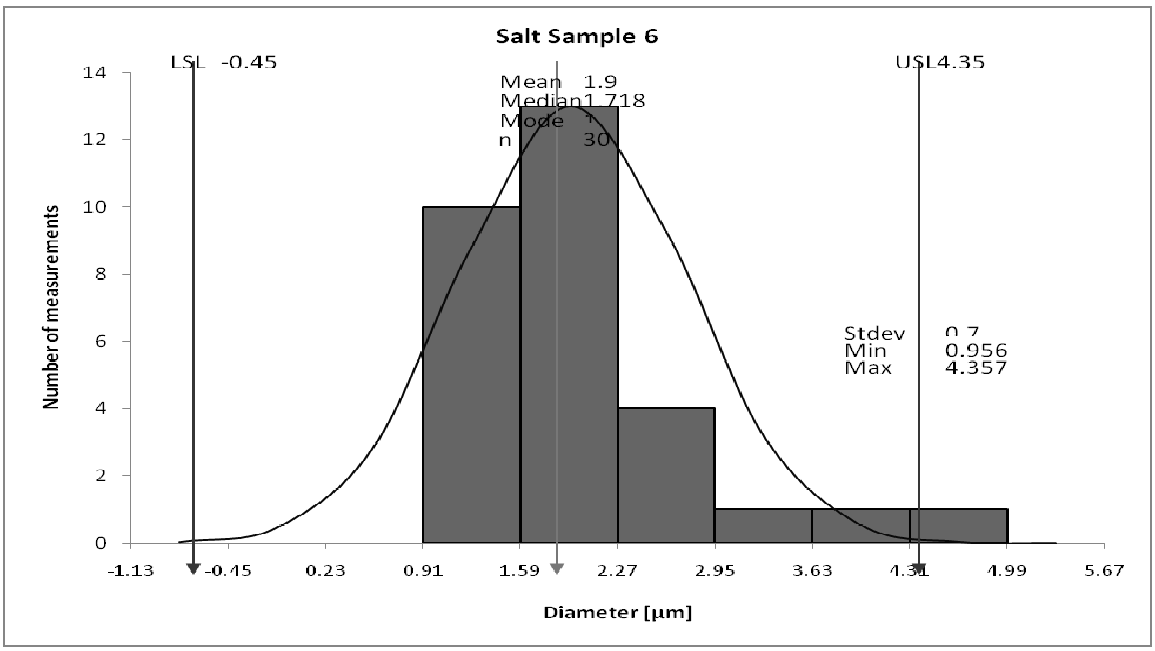
Graph 5.3: Sizes of particles of sample 3 of spray dried sodium chloride



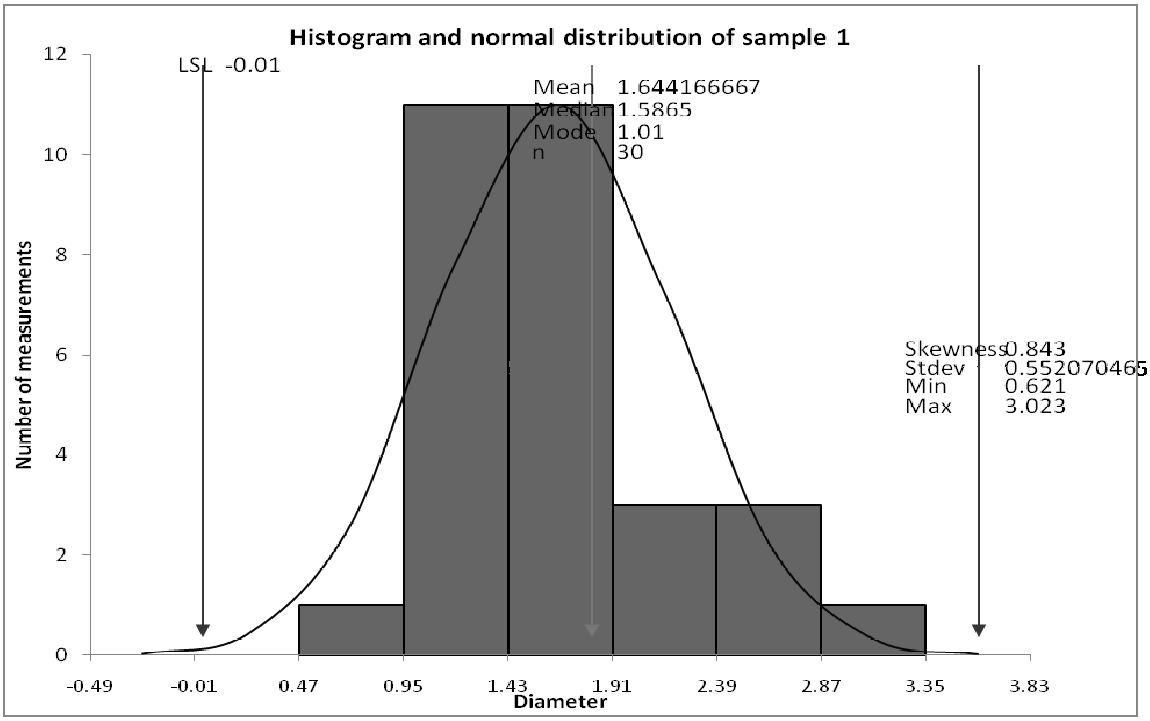
Graph 5.4: Sizes of particles of sample 4 of spray dried sodium chloride



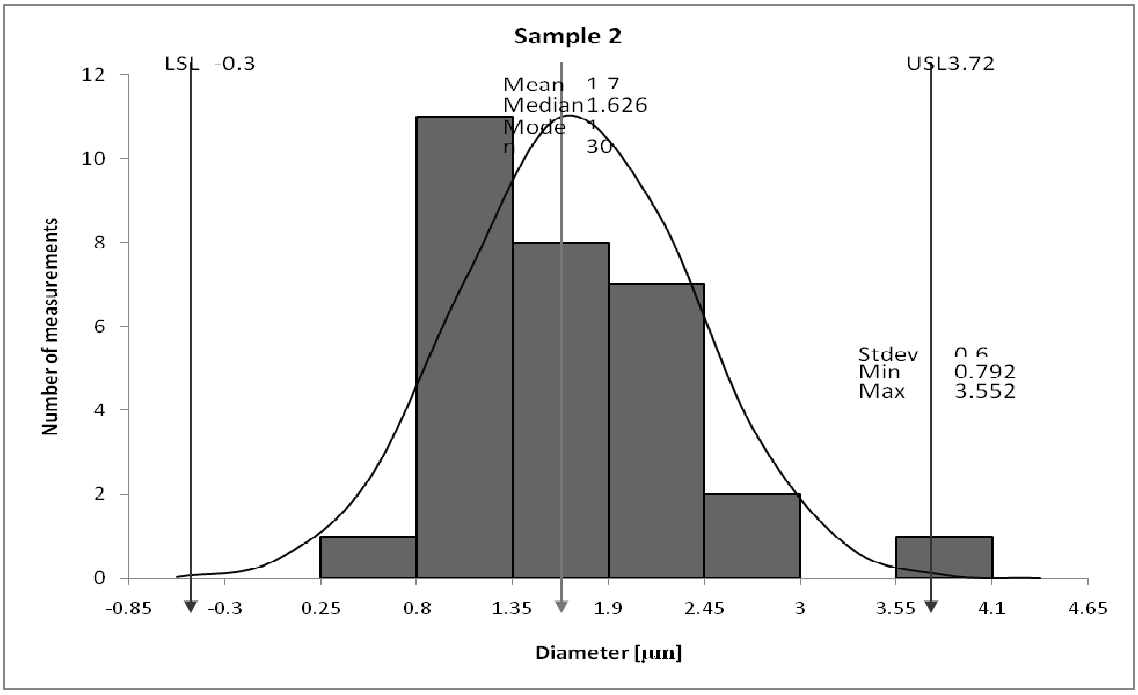
Graph 5.5: Sizes of particles of sample 5 of spray dried sodium chloride



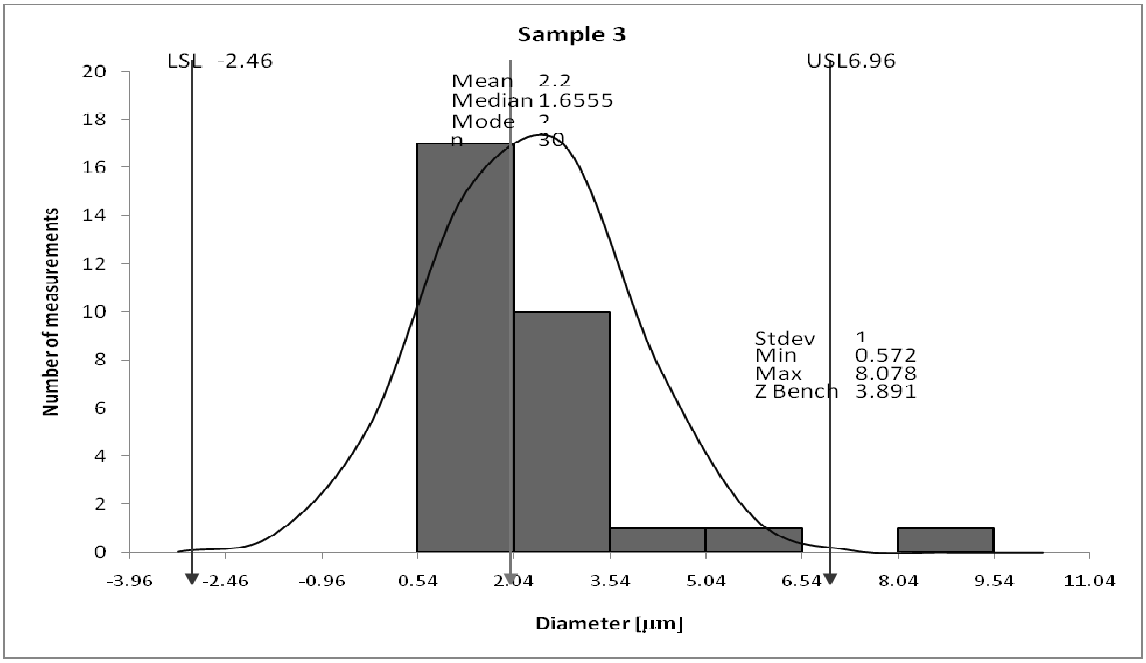
Graph 5.6: Sizes of particles of sample 6 of spray dried sodium chloride



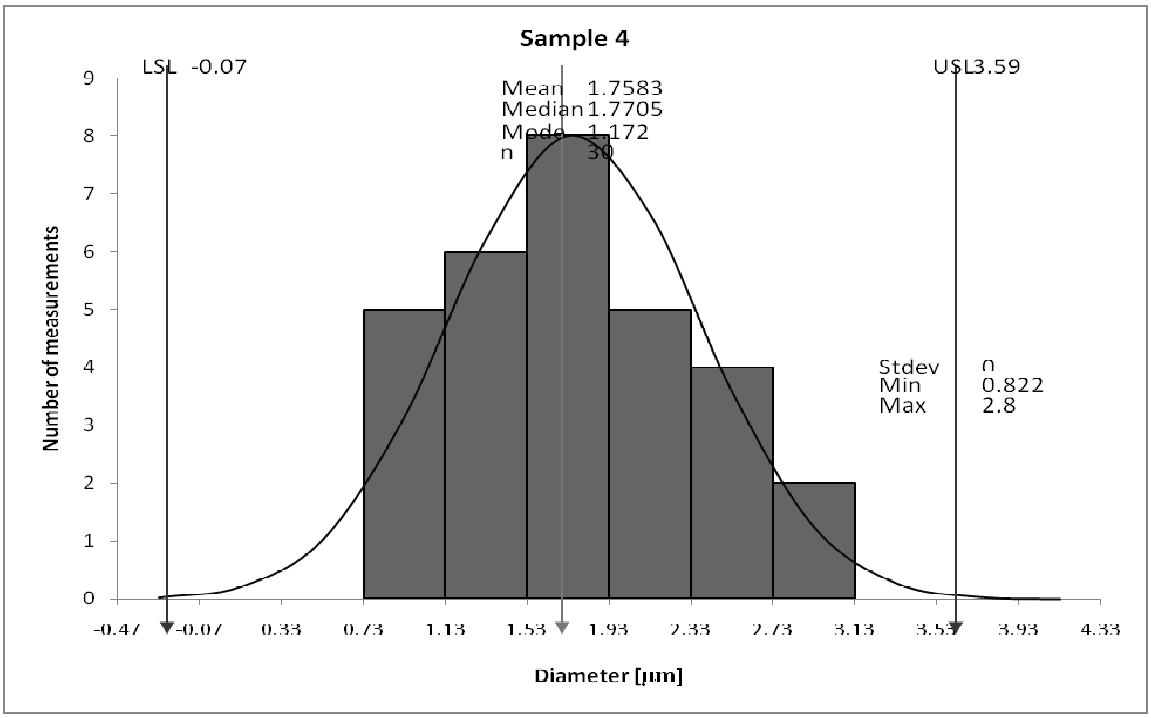
Graph 5.7: Diameter of microcapsules of sample 1 of encapsulated PCM



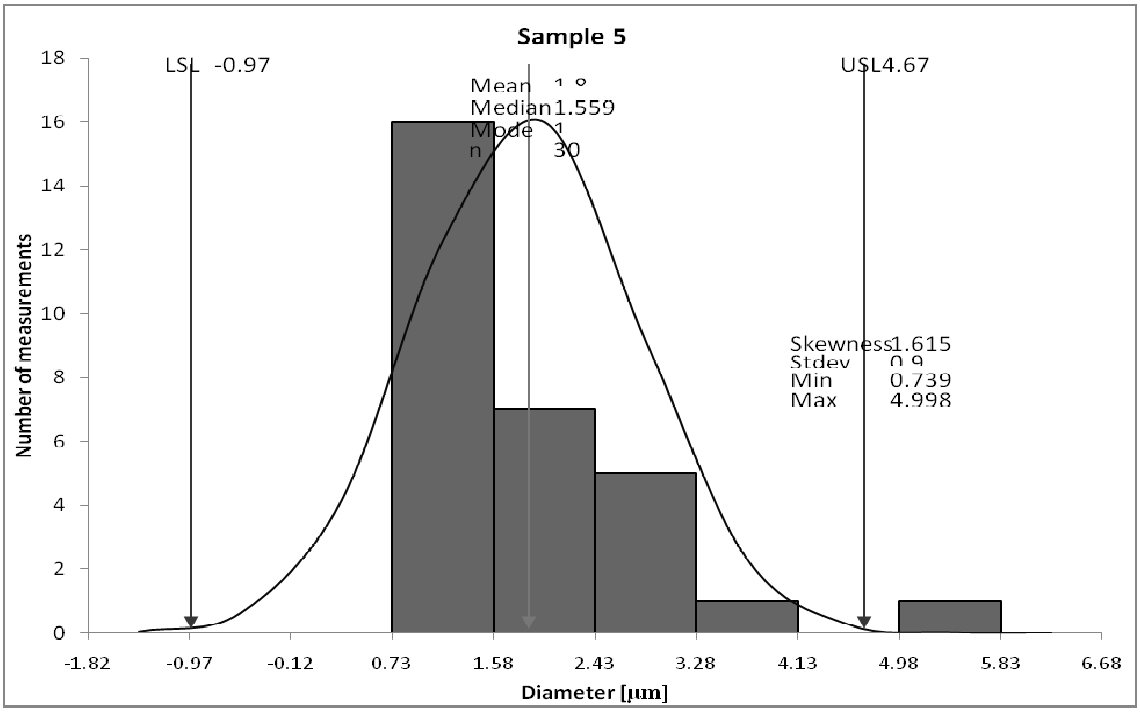
Graph 5.8: Diameter of microcapsules of sample 2 of encapsulated PCM



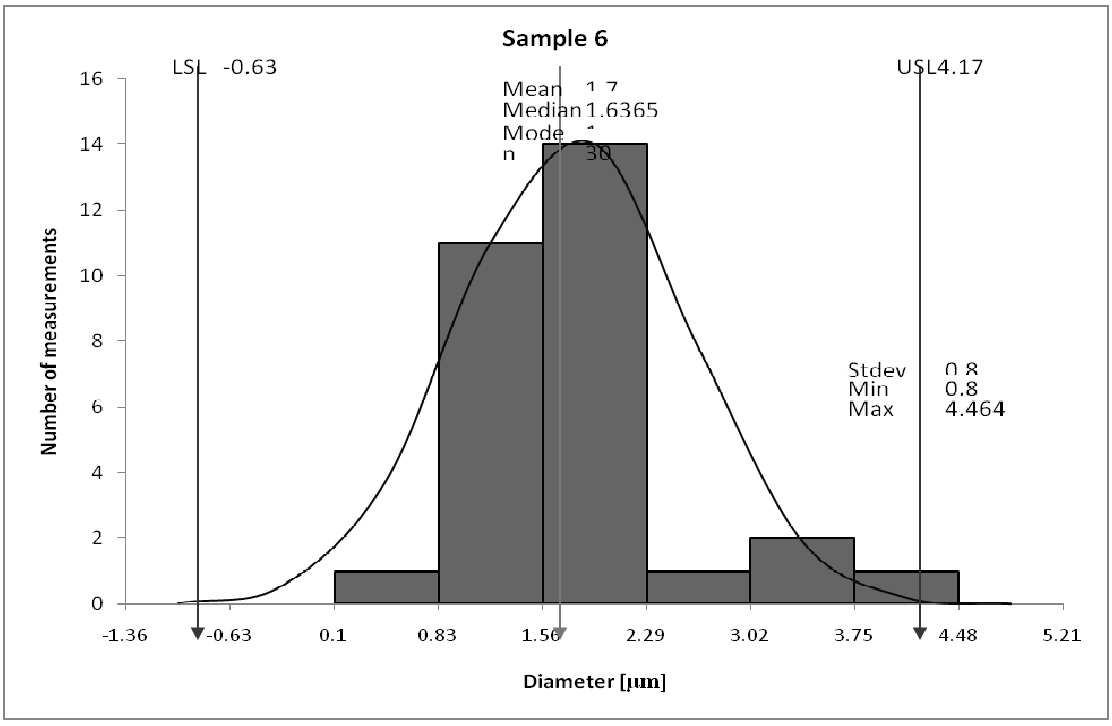
Graph 5.9: Diameter of microcapsules of sample 3 of encapsulated PCM



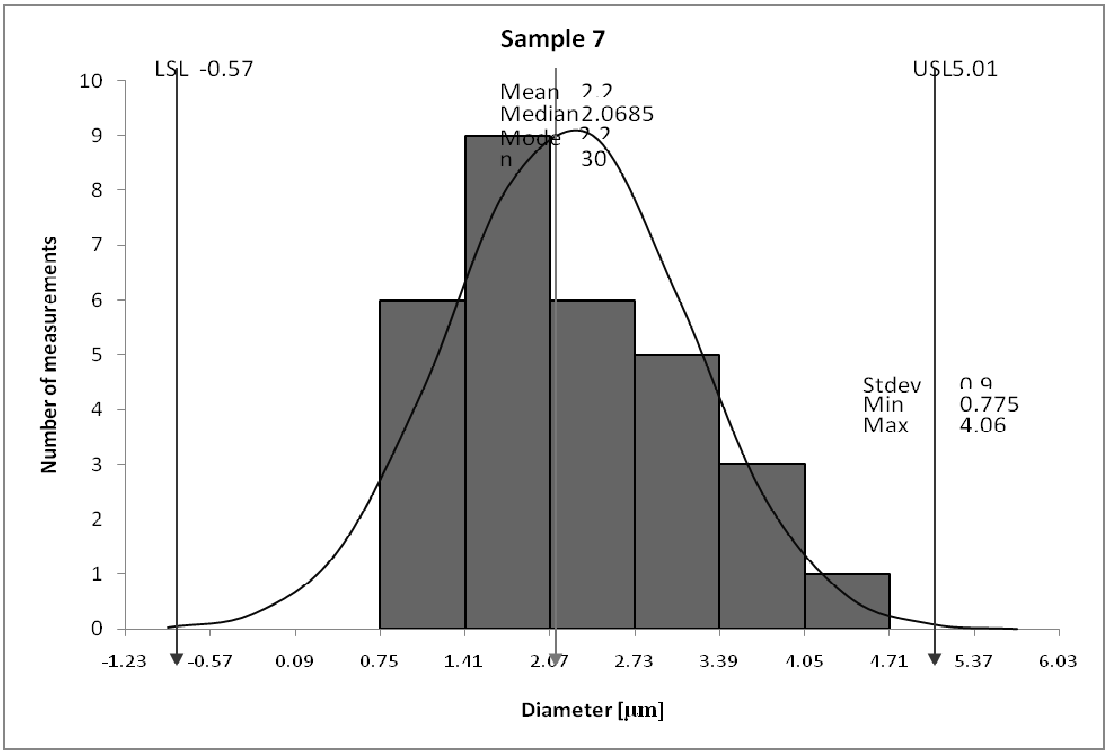
Graph 5.10: Diameter of microcapsules of sample 4 of encapsulated PCM



Graph 5.11: Diameter of microcapsules of sample 5 of encapsulated PCM



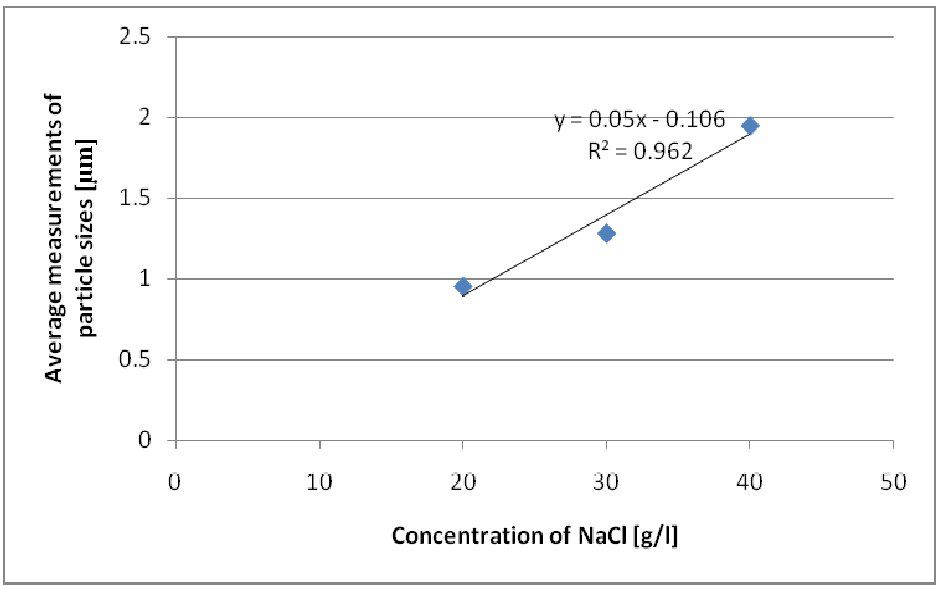
Graph 5.12: Diameter of microcapsules of sample 6 of encapsulated PCM



Graph 5.13: Diameter of microcapsules of sample 7 of encapsulated PCM

6. Conclusion

Creation of micro-particles was achieved through using of spray drying process. Spray dried salt powder containing micro-particles was measured, where it was shown that the spray drying parameters showed influence in the particle sizes. Inlet temperature of the spray dryer had variable effect in the particle sizes. Solid concentration had an influence in the particle sizes, the addition of solid (salt) concentration caused an increase in the size of particles.



The smallest micro-particle sizes were chosen for application on fibers surfaces. These particles were able to penetrate the fiber surface due to their small sizes. When 10 % w/w of NaCl powder was applied to the fiber sample, the micrographs showed a rough fiber surface whereas the usage of 1 % w/w NaCl showed breakage on the surfaces.

The fibers sample that were applied with the same percentage of salt powder as explained in the above treated samples, this samples were dried and washed off with distilled water to the difference between the two processes. The micrographs of fiber samples with 10 % w/w of NaCl appeared to have opening and particles fixed into the fiber. The fiber sample with 1 % w/w had rough surfaces.

Fiber samples with 10 % w/w of NaCl showed more damages of fiber surface compared to sample with 1 % w/w NaCl. Fibers sample that were washed with water appeared to have more opening and traces of particle inside the fiber compared to the fiber sample without washing.

The second part of application of salt powder on fiber samples was by fixing the fibers inside the spray dryer so the particles can be attached straight to the fibers sample during spray drying process. Through observation, the fibers that were dried only showed openings and traces of particles on the openings of the fiber surface. The washed samples appeared to have opening without traces of particles and had more ruptures and damages on the fiber surface.
Washing of fiber samples after application of spray dried powder containing micro-particles causes more openings on the fiber surface thus leading to fiber damages. Usage of higher temperatures for drying the sample has no effect as traces of particles are present and also the damages of fiber is not affected.

Due to high demand of polyester fibers around the continent, because of its better properties (mechanically, physical & chemically) this is the reason why I decided to use it in my experiments. The application of small amount of salt (NaCl) through spray drying in the fiber enables to damage the fiber by cracking it or creating opening on the fiber. Polyester fibers are difficult to dye, so by creating cracks or fractures on the fiber makes it easier to dye them because of these porous structures. These pores will absorb the dye with the help of alkaline solution; the dye will be then fixed into the fiber. Polyester fiber is covered by modified polyester fiber (copolyester) which is known for being capable of improving dyeability. The polyester and modified fibers dye readily with disperse dyes. Openings and cracks on the fiber surface not only improve dyeability but water absorption as well.

In the preparation of Phase Change Materials, using high content of water increases the mean diameter of micro-capsules. The high quantity of paraffin wax reduces the mean diameter of microcapsules. The smaller quantity of wall material (gelatin & gum arabic) gives high mean diameter of microcapsules which then gives the material better properties. Application of encapsulated phase change material on textile material was unsuccessful. This was due to the emulsion of encapsulated powder in the finishing bath that contained cross linking agents and binder. The micrographs of the treated sample did not show any traces of microcapsules.

7. List of literature

[1] Arshady R. Manufacturing Methodology of microcapsules. MML Series. Volume 1: Preparation & Chemical Applications (Microspheres, Microcapsules & Liposomes).Citrus Books 1999, pg 279

[2] Microtek laboratories Inc: Technical overview of microencapsulation, copyright 2009. Website address: <http://www.microteklabs.com/technical_overview.html > Date: March 2009

[3] Rouette H. Encyclopedia of textile finishing, Springer, autumn 2000

[4] Meyvis T. Microencapsulation technology for coating and laminating. Laboratorium Gent .Unitrex 6-2001, pg 13

[5] Somasundaran P. Encyclopedia of surface and colloid science, CRC Press 2006, pg 3957

[6] Benita S. Microencapsulation: methods and industrial applications, CRC Press 2006, Volume 158, ISBN 0824723171. Pg 113

[7] Bete Fog Nozzle Inc. Spray dry manual. Website address: <http://www.bete.com/pdfs/BETE_SprayDryManual.pdf>

[8] BÜCHI Labortechnik AG, Mini Spray Dryer B-290 Website address: < http://webmaster.buchi.com/Mini-Spray-Dryer-B-290.179.0.html> Date: October 2009

[9] Bansode S. Microencapsulation: A Review. International Journal of Pharmaceutical Sciences Review and Research, Volume 1, Issue 2, March 2010, Article 008, pg 38, ISSN 0976– 044X

[10] Laboratory-scale spray dryer. Wikipedia. March 2007. Website address: <http://en.wikipedia.org/wiki/File:Labspraydryer.jpg> Date: October 2009

[11] Nelson G. Application of microencapsulation in textiles, International Journal of Pharmaceutics 242, 2002, pg 59-60

[12] Ghosh S.K. Functional coatings: by polymer microencapsulation, Die Deutsche bibliothek, 2006, pg 233, ISBN 352731296

[13] Dubey R. Microencapsulation Technology and Application, Defence Science Journal, Vol 59, No. 1, January 2009, pg 82

[14] Mehling H. Heat and Cold Storage with PCM: An Up to Date Introduction into Basics and application, Springer 2008, pg 37, ISBN 9783540685562

[15] Castellón C. Use of Microencapsulated Phase Change Materials in Building Applications, 2007, Website address: <http://www.ornl.gov/sci/buildings/2010/Session%20PDFs/35_New.pdf> Date: January 2010

[16] Tomasino C. Chemistry and technology of fabric preparation and finishing, Raleigh, North

Carolina, 1992, pg 38

[17] Doshi G. Phase change material in Textiles, Ezine Articles, copyright 2006, Website address: <http://ezinearticles.com/?Pcm-In-Textiles&id=367030> Date: March 2010

[18] Shim H. Using Phase Change Materials in Clothing, Institute for Environmental Research, Kansas State University, Textile Research Journal 71, No: 6, 2001, pg 495

[19] Militky J, Textile science and technology: Modified Polyester Fibers, Volume 10, pg 34 & 97

[20] Hegde R. Bicomponent fibers, April 2004, Website address: <http://www.engr.utk.edu/mse/Textiles/Bicomponent%20fibers.htm> Date: January 2010

[21] Lewin M. Handbook of fiber chemistry, third edition, CRC Press, 2007, pg 122, ISBN 0824725654

[22] Mcintyre J. Synthetic fibers: nylon, polyester, acrylic, polyolefin, Wood head Publishing Ltd and CRC Press LLC, 2005, p 94, ISBN 0849325927

[23] Raghavendra R. Polyester fibers, April 2004, Website address: <http://web.utk.edu/~mse/pages/Textiles/Polyester%20fiber.htm> Date: February 2010

[24] Clugston M. Advanced Chemistry, Oxford University Press, 2000, pg 34, ISBN 019914633

[25] Hein M. Foundation of college chemistry, Alternate thirteenth edition, Wiley Publishers, 2000, pg 220, ISBN 139780470460603

[26] Jim Schweitzer. Scanning electron microscopy, Purdue University: Radiological & Environmental Management, Modified October 2006, Website address: <http://www.purdue.edu/REM/rs/sem.htm> Date: March 2009

[27] Joseph I, Scanning Electron Microscopy and X-Ray Microanalysis, 3rd Edition. Kluwer Academic/Plenum Publishers, New York, 2003, pg 689, ISBN 0-306-47292-9

8. List of Appendinces

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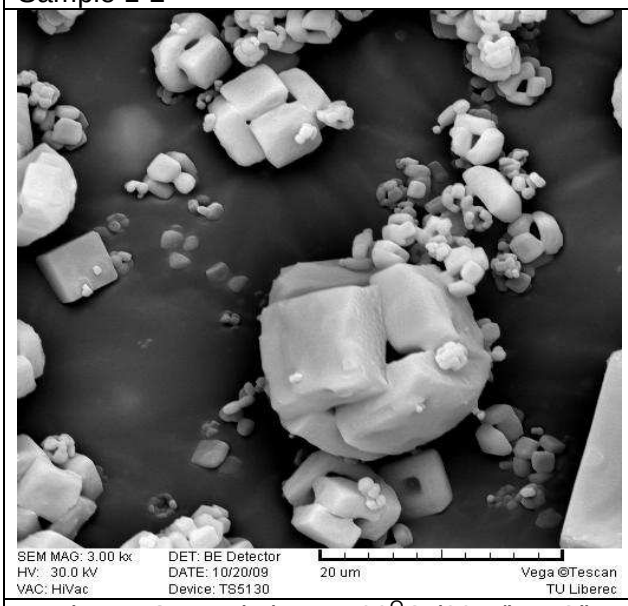
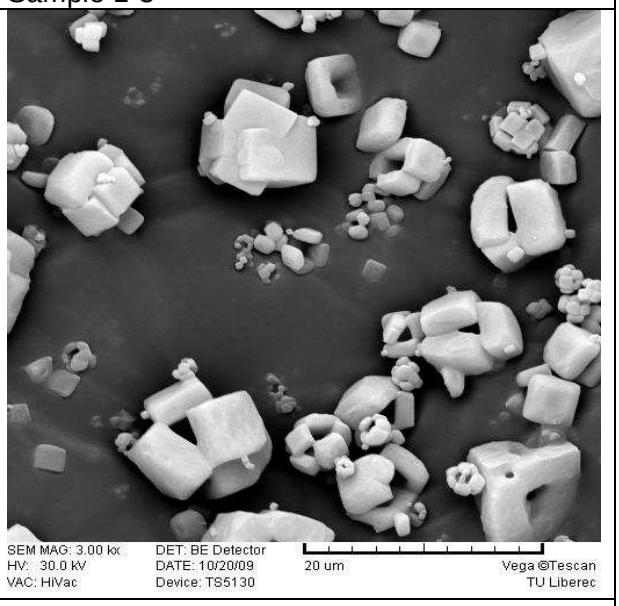
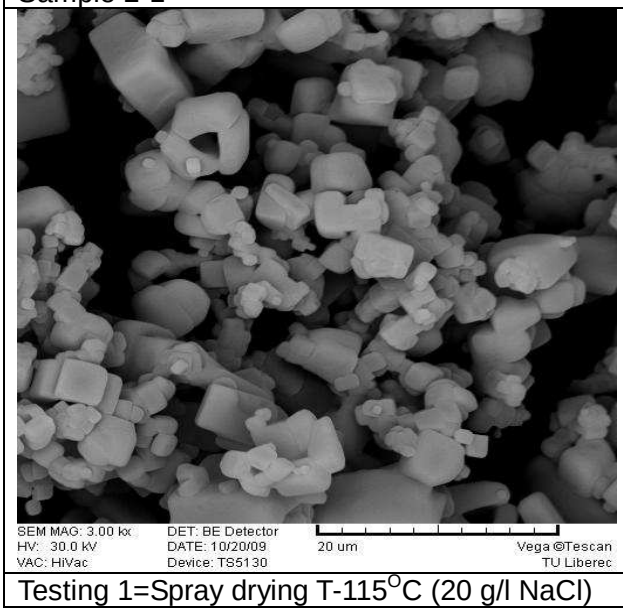
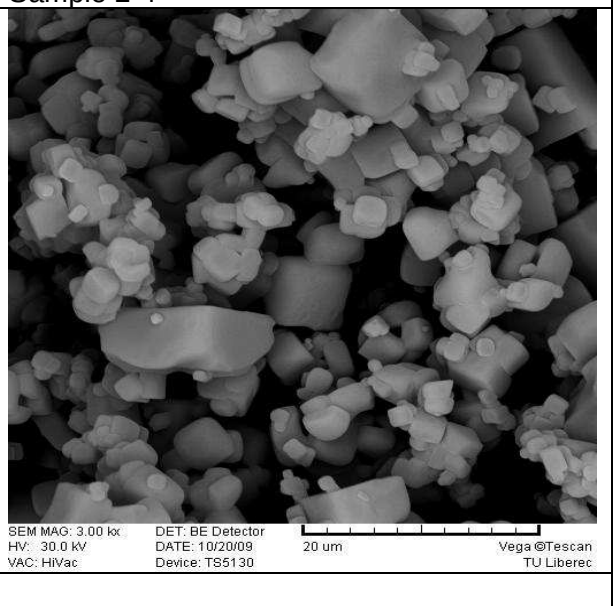
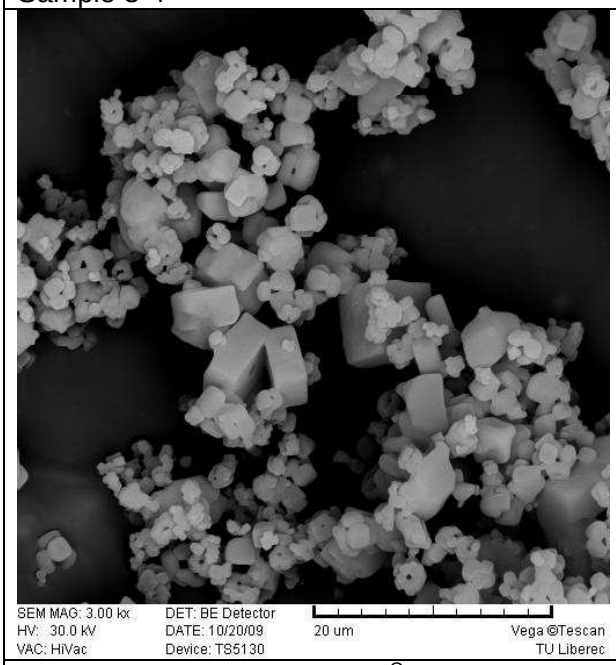
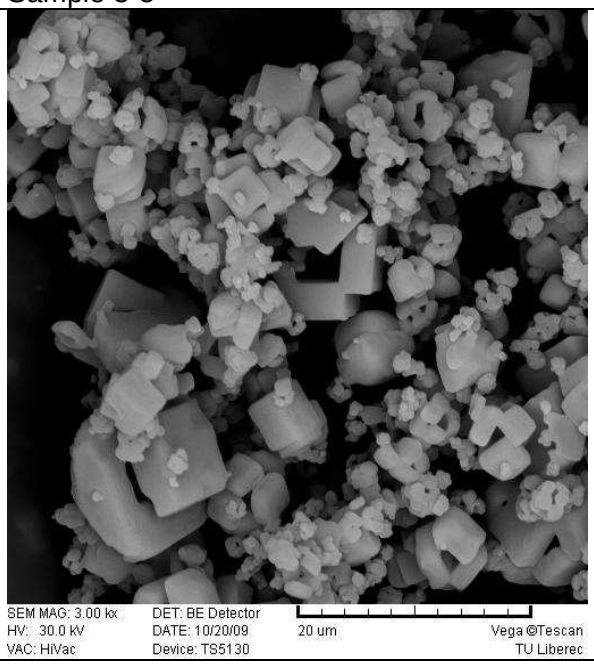
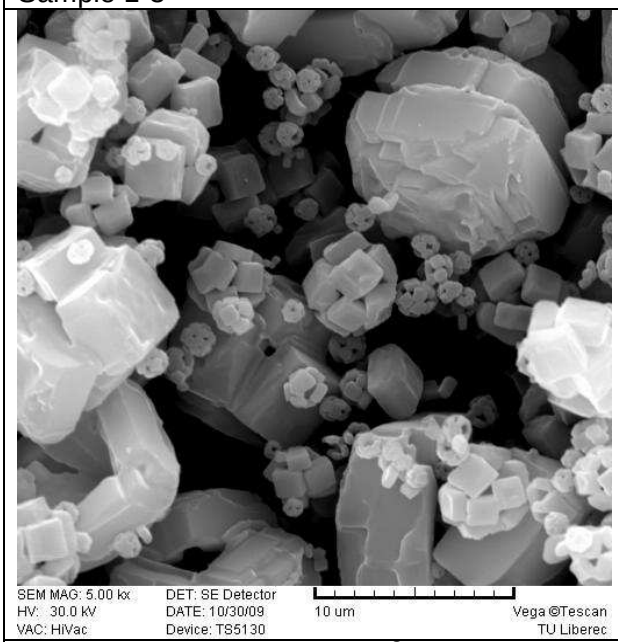
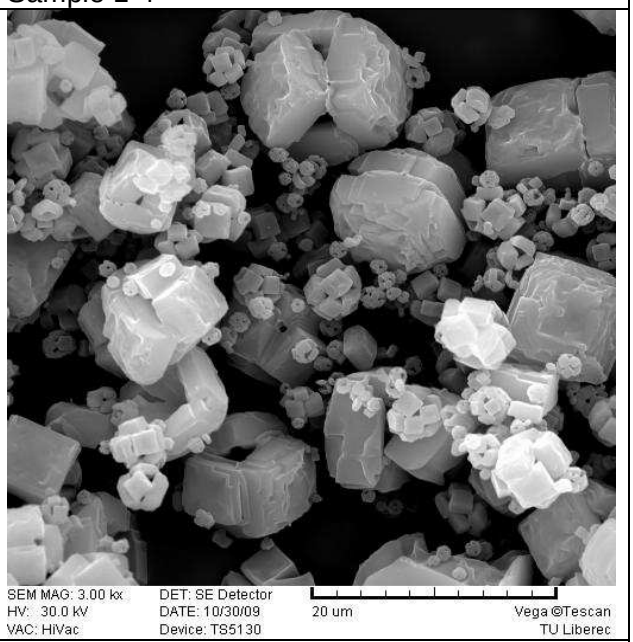
Appendix 1: First testing of spray dried sodium chloride

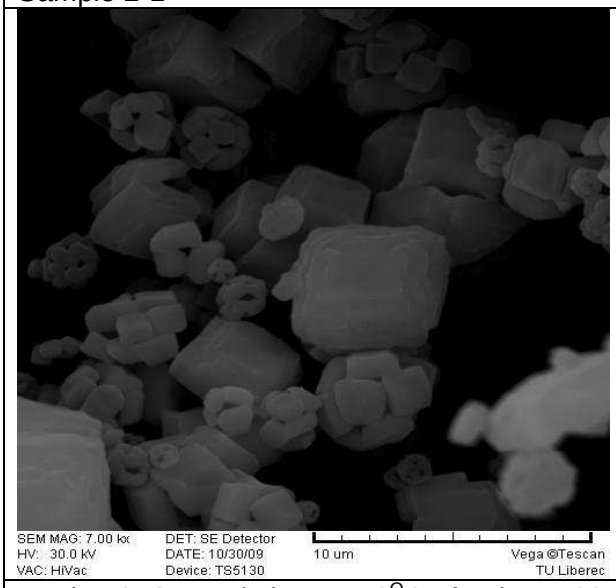
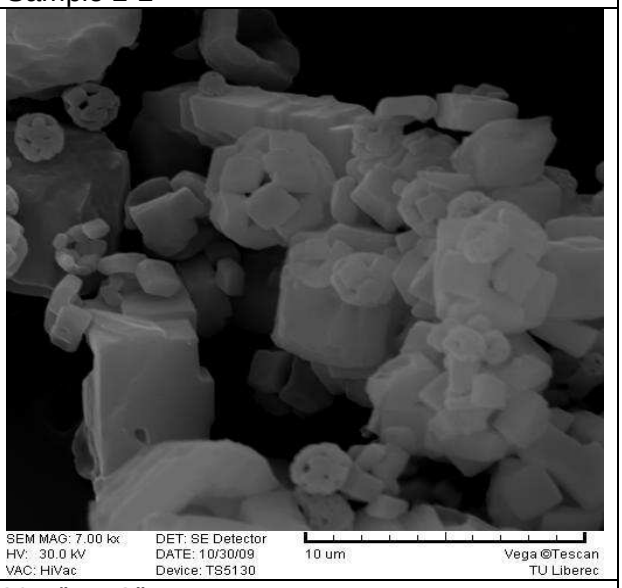
Sample 1-2	Sample 1-3
	
Testing 1=Spray drying T-100^{O}C (20 g/l NaCl)	

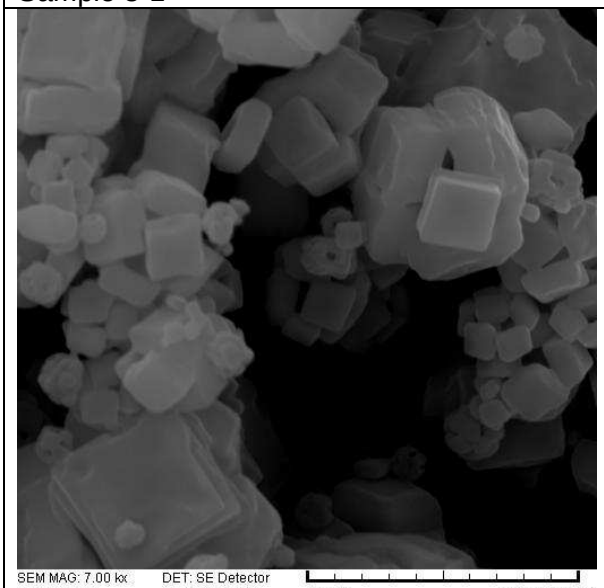
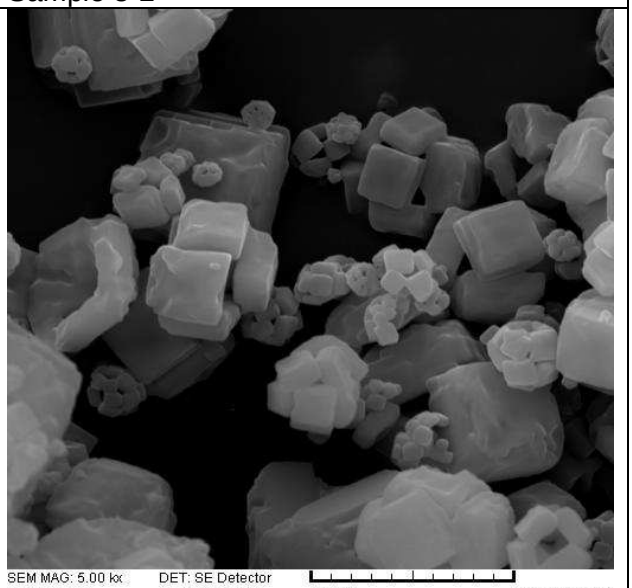
Sample 2-1	Sample 2-4
	
Testing 1=Spray drying T-115^{O}C (20 g/l NaCl)	

Sample 3-4	Sample 3-5
	
Testing 1=Spray drying T-130^{O}C (20 g/l NaCl)	

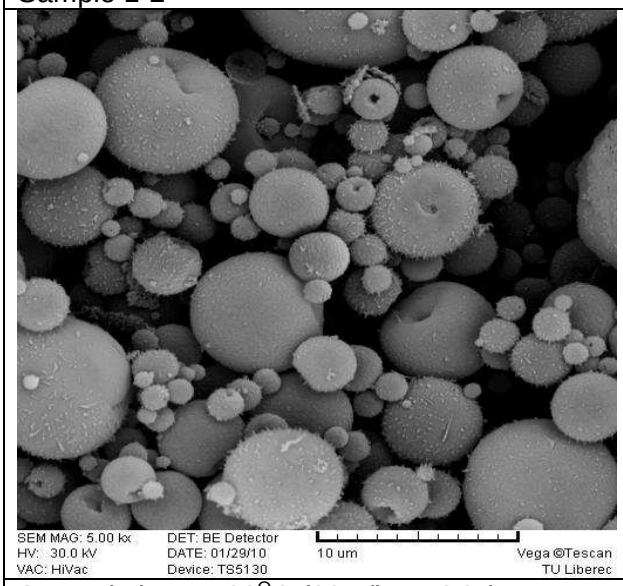
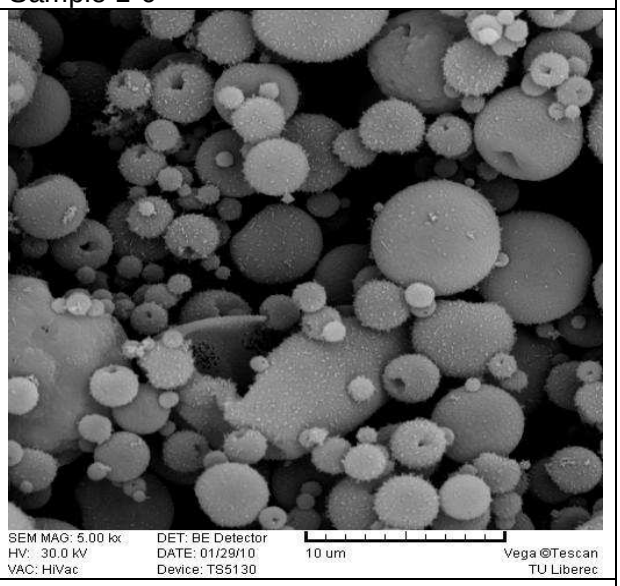
Appendix 2: Second testing of spray dried sodium chloride

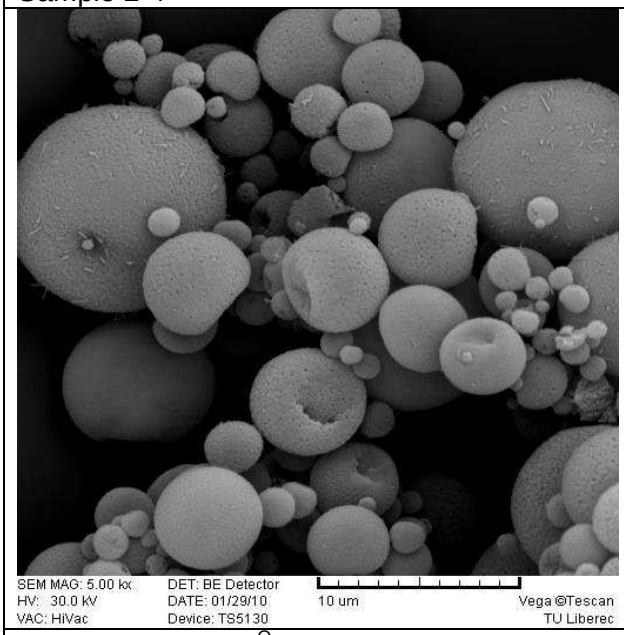
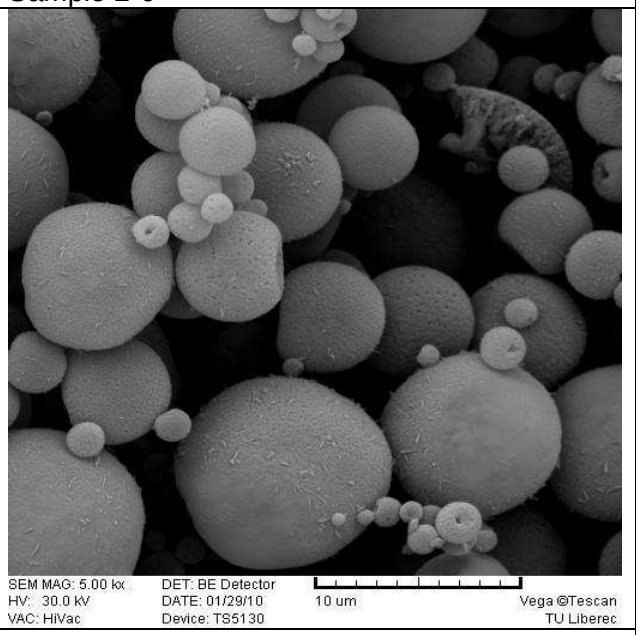
Sample 1-3	Sample 1-4
	
Testing 2=Spray drying T-140^{O}C , feed rate-15, (20 g/l NaCl)	

Sample 2-1	Sample 2-2
	
Testing 2=Spray drying T-140^{O}C , feed rate-20, (20 g/l NaCl)	

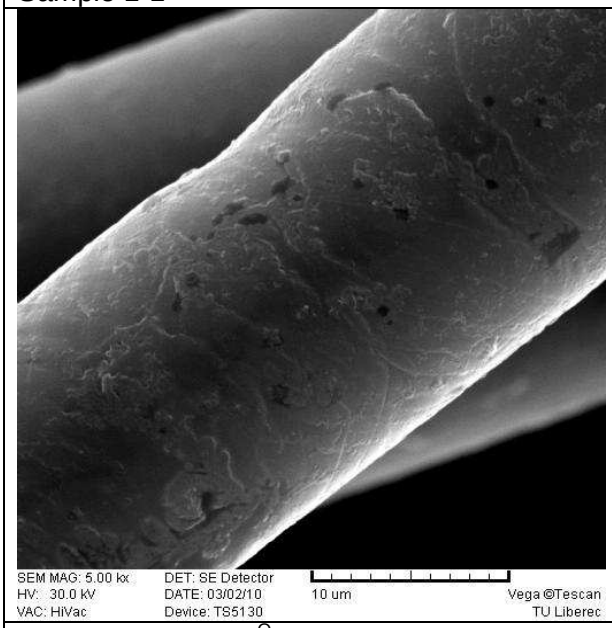
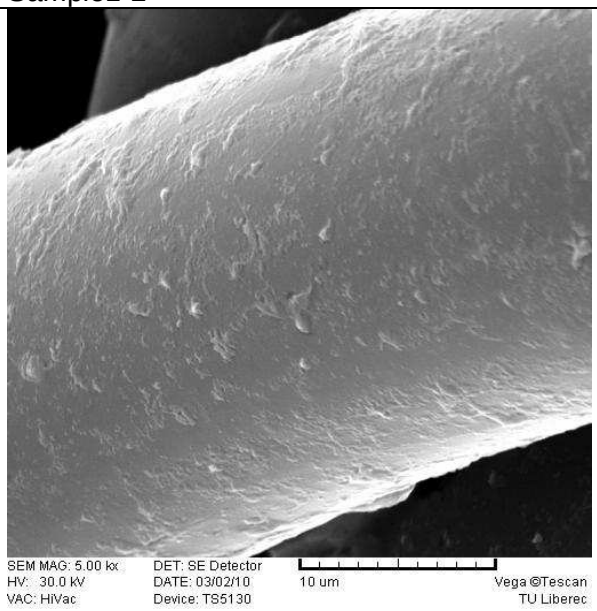
Sample 3-1	Sample 3-2
	
Testing 2=Spray drying T-140^{O}C , feed rate-25, (20 g/l NaCl)	

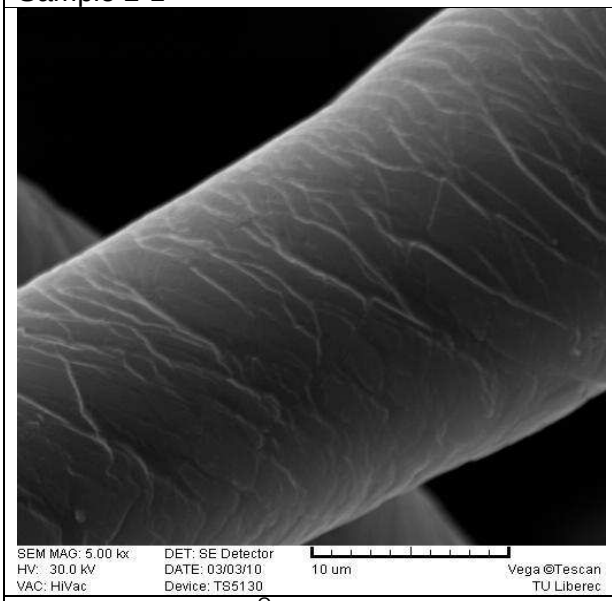
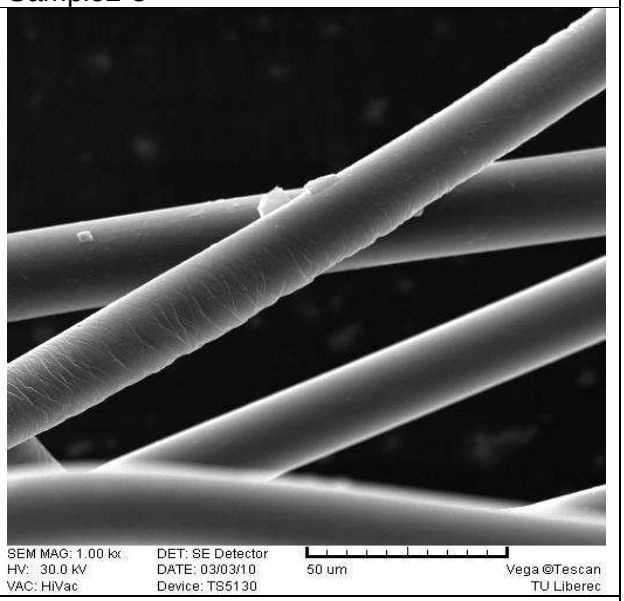
Appendix 3: Spray dried sodium carbonate

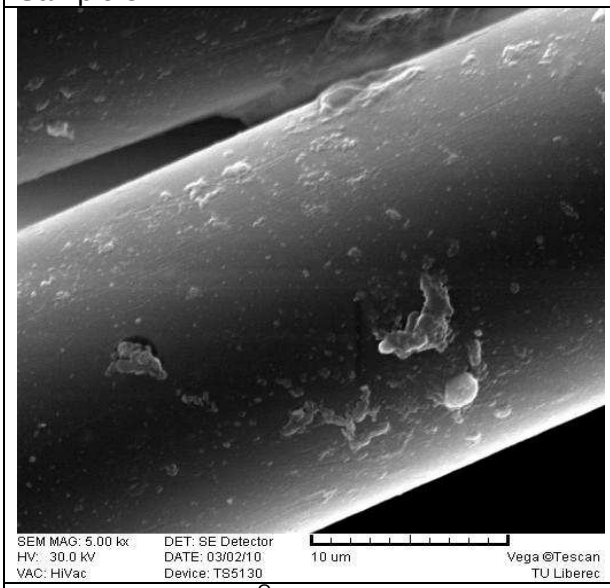
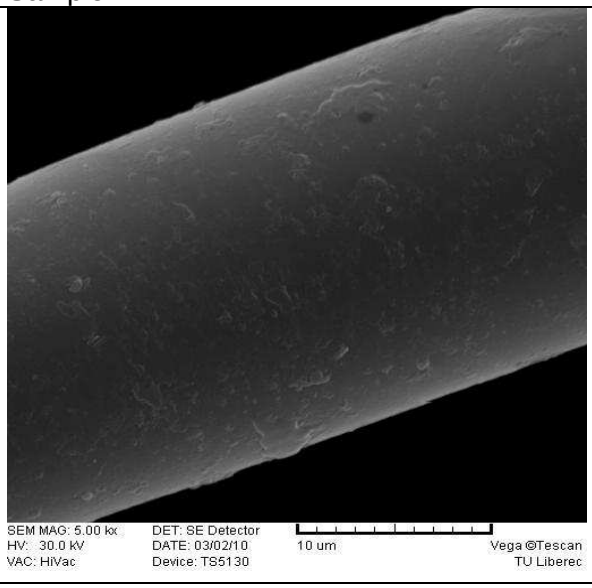
Sample 1-2	Sample 1-6
	
Spray drying T-180^{O}C (20 g/l Na_2CO_3)	

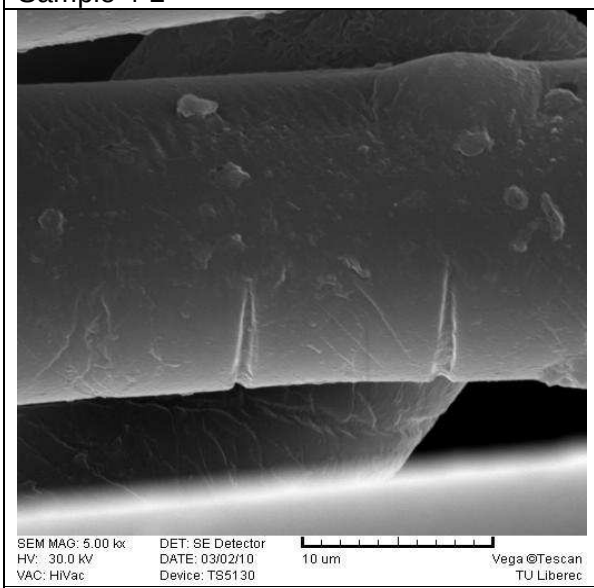
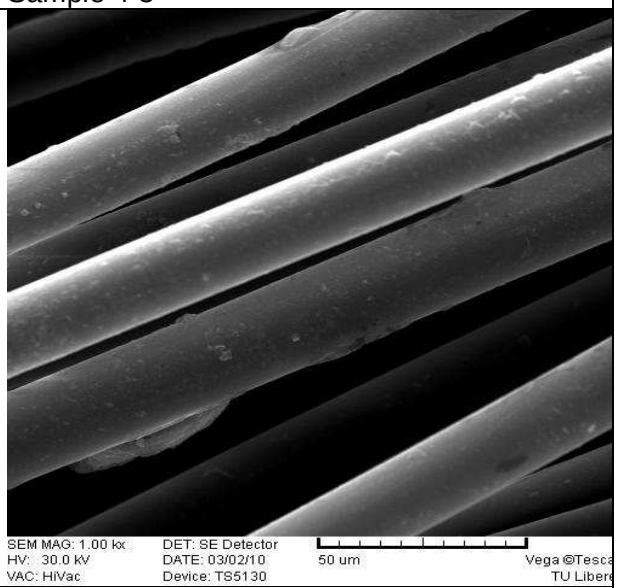
Sample 2-4	Sample 2-6
	
Spray drying T-200^{O}C (20 g/l Na_2CO_3)	

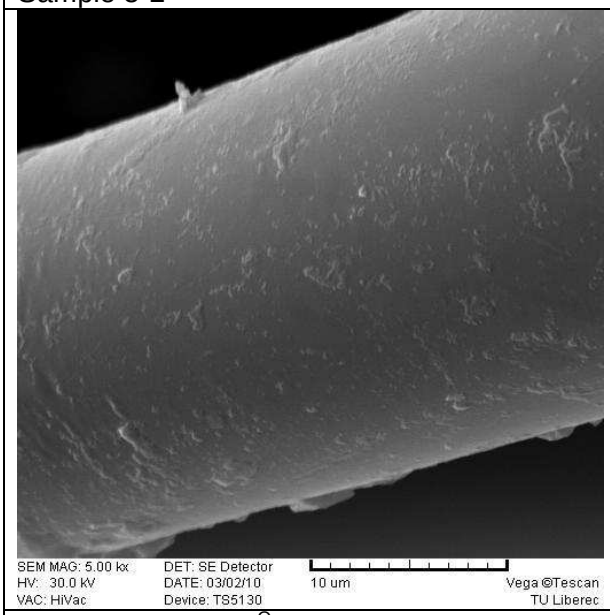
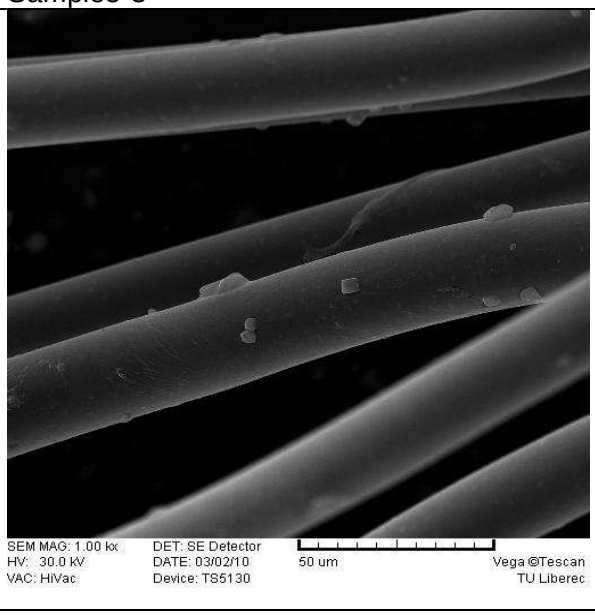
Appendix 4: First application of spray dried powder on bicomponent fibers by friction

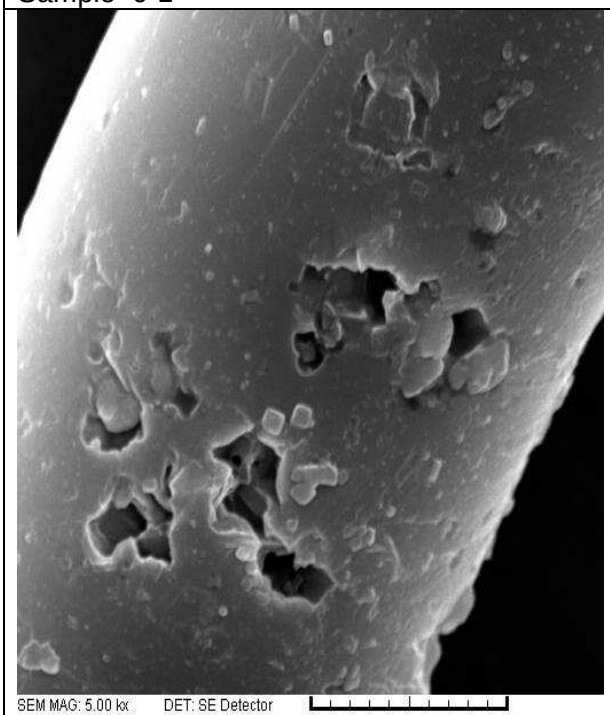
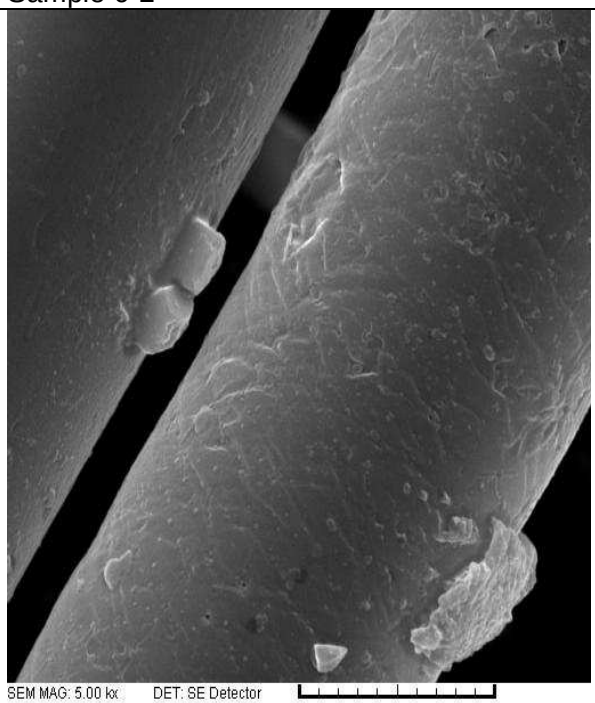
Sample 1-1	Sample1-2
	
Spray drying T-180^{O}C, drying of sample (only drying)	

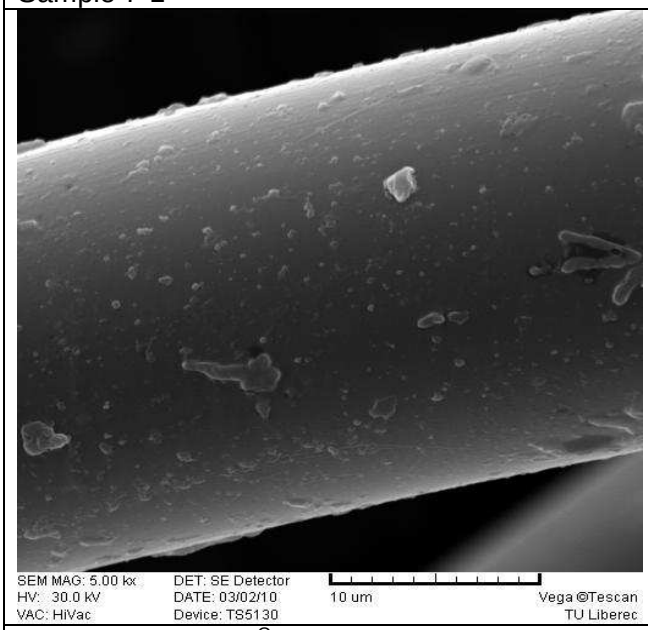
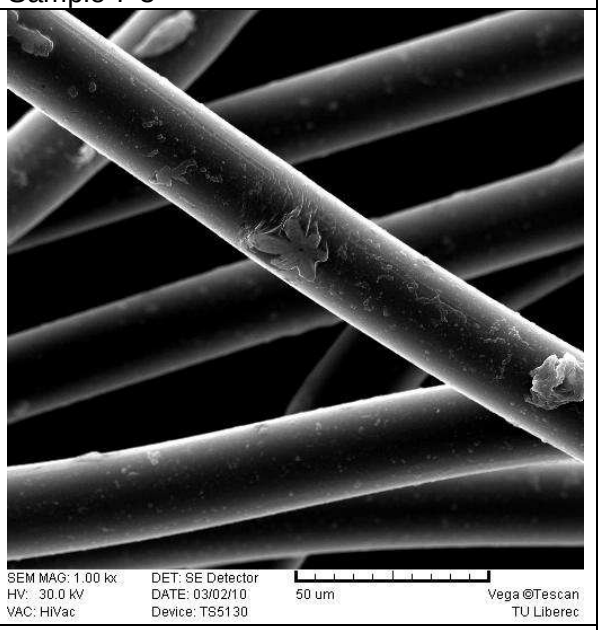
Sample 2-1	Sample2-3
	
Spray drying T-200^{O}C, drying of sample (only drying)	

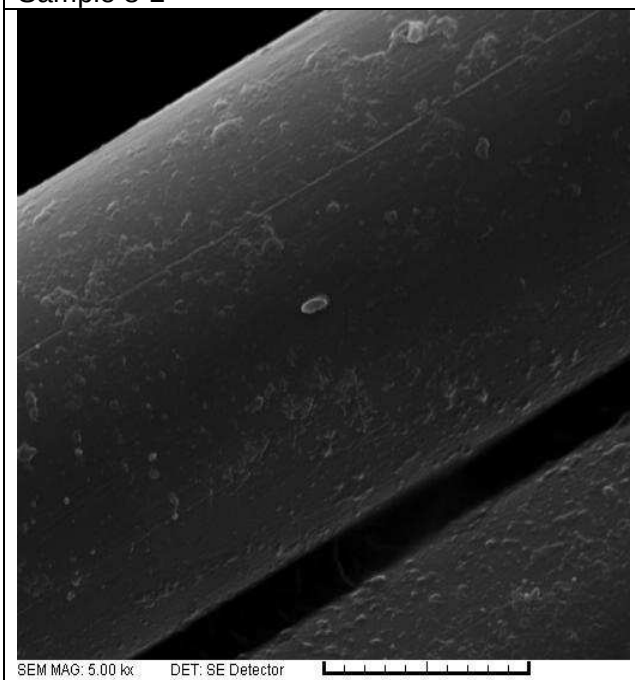
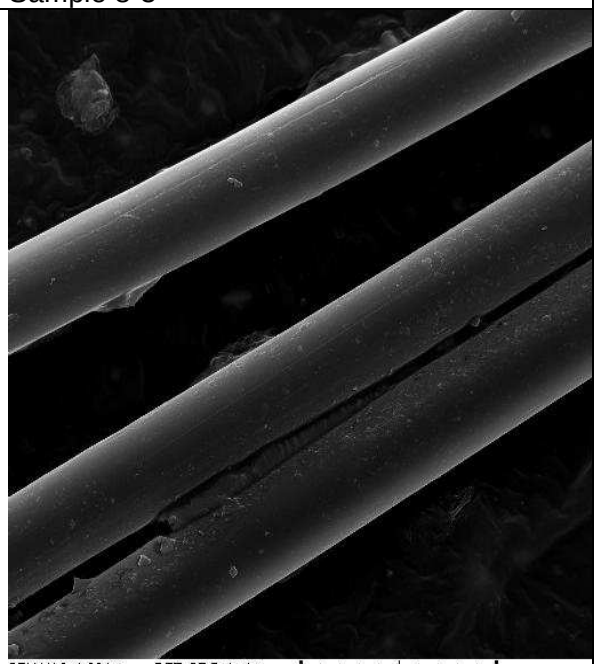
Sample 3-1	Sample4-1
	
Spray drying T-180^{O}C, drying of sample (only drying)	

Sample 4-2	Sample 4-3
	
Spray drying T-200^{O}C, drying of sample (only drying)	

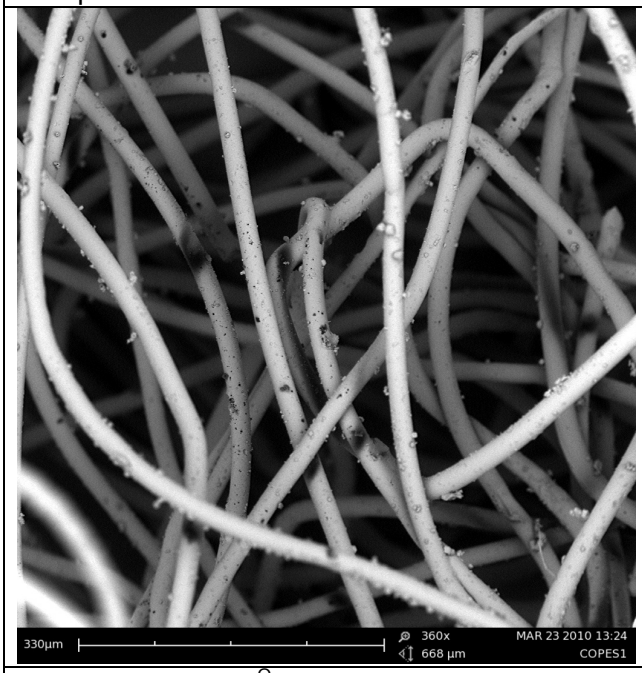
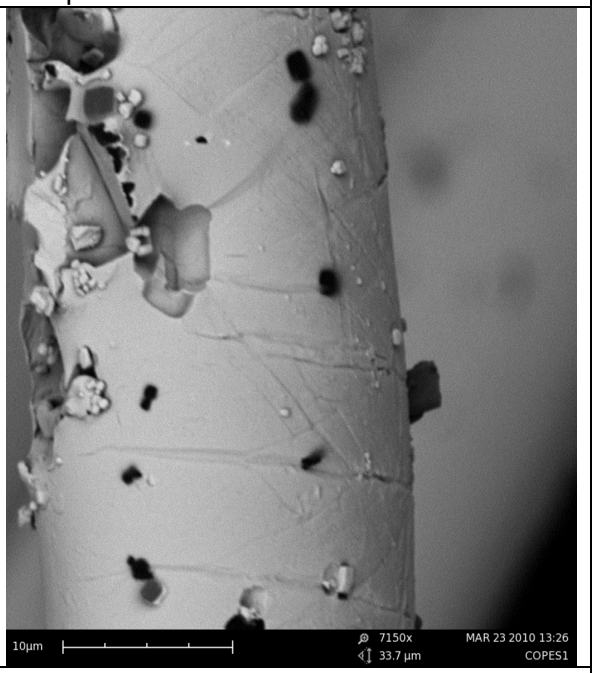
Sample 5-2	Sample5-3
	
Spray drying T-180^{O}C, drying of sample (washing of samples)	

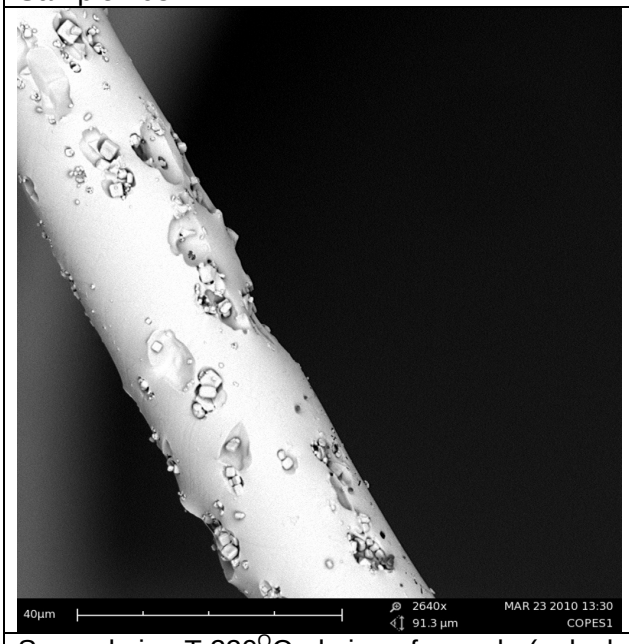
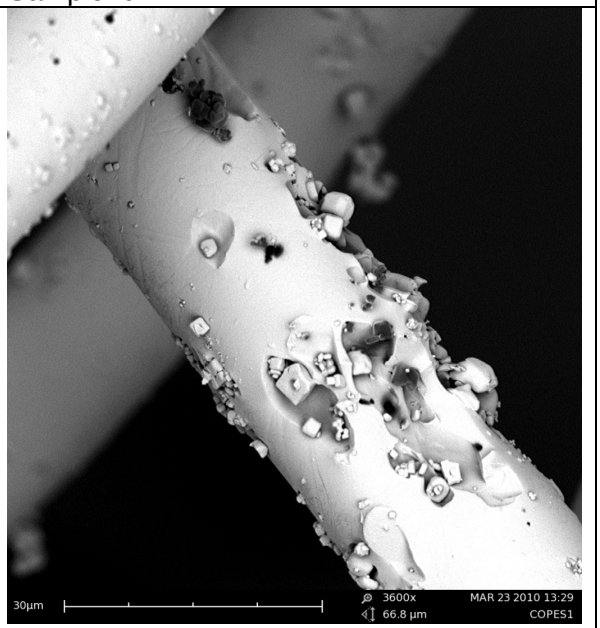
Sample 6-1	Sample 6-2
	
Spray drying T-200^{O}C, drying of sample (washing of samples)	

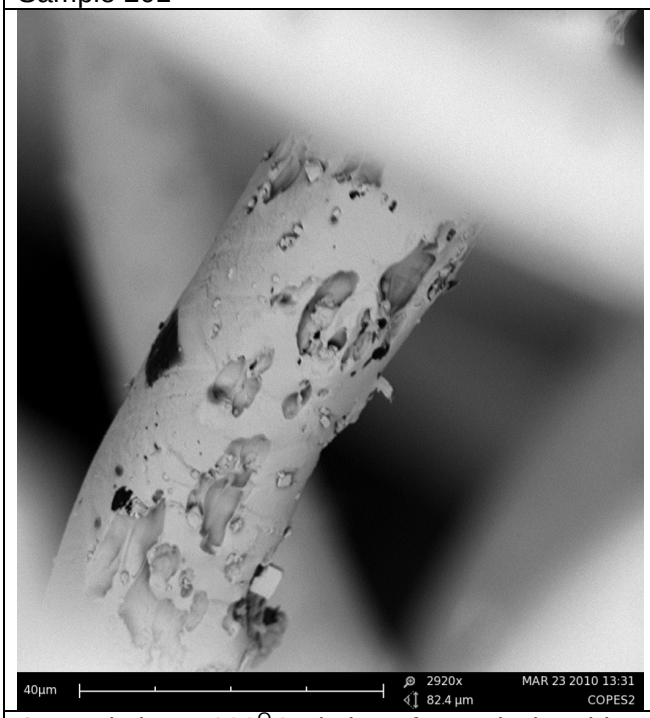
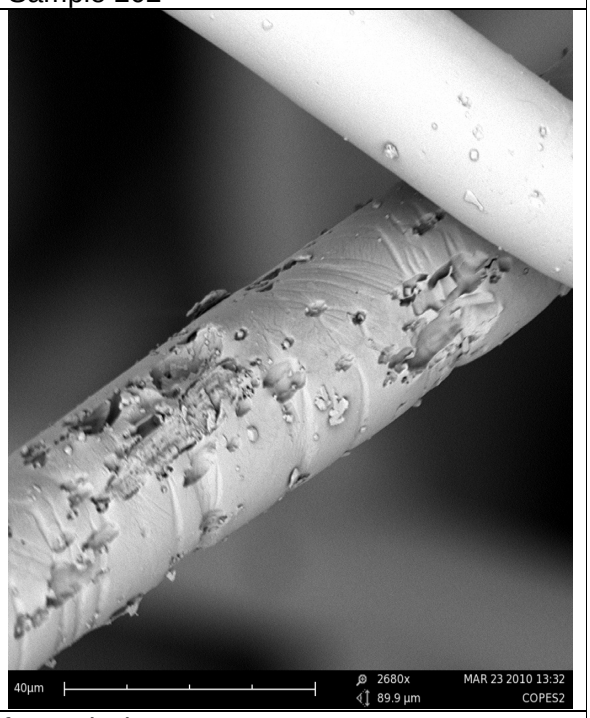
Sample 7-1	Sample 7-3
	
Spray drying T-180^{O}C, drying of sample (washing of samples)	

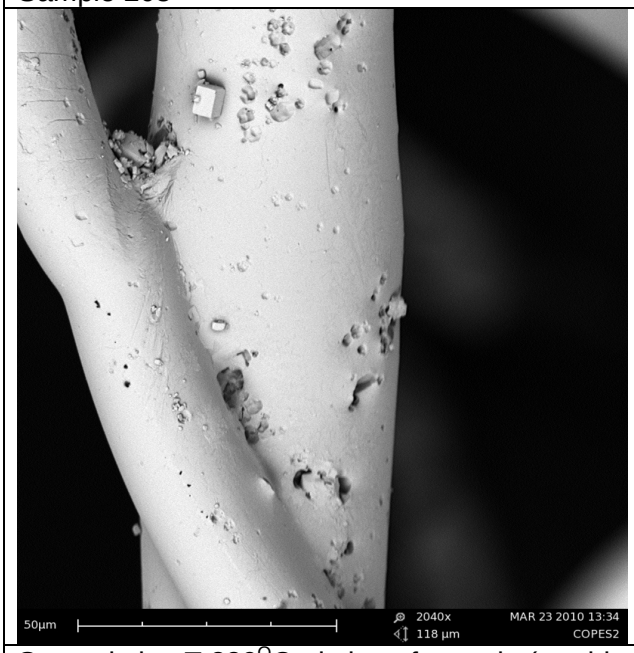
Sample 8-2	Sample 8-3
	
Spray drying T-200^{O}C, drying of sample (washing of samples)	

Appendix 5: First application of sodium chloride directly on bicomponent fibers by drying

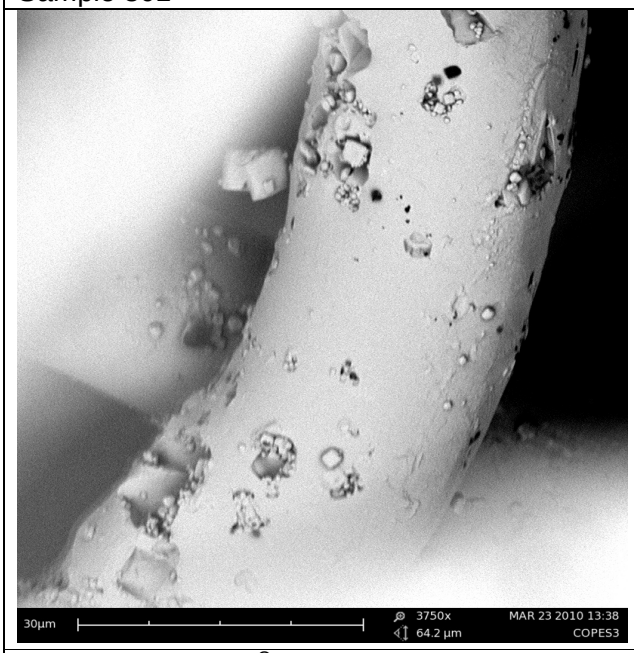
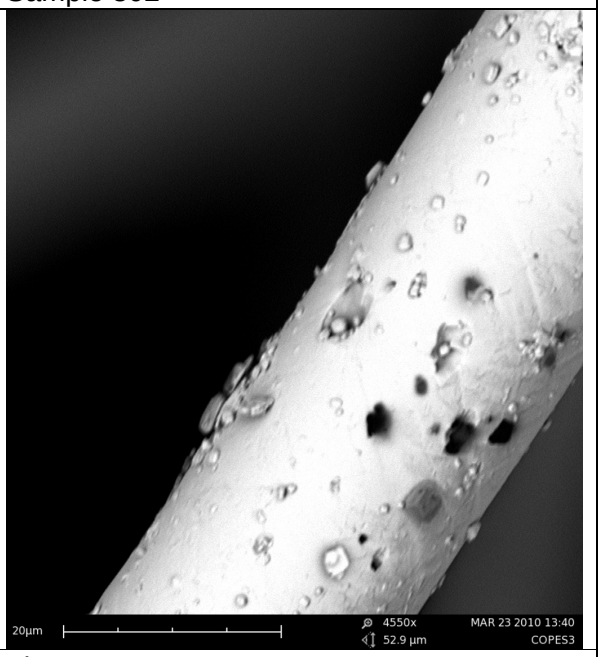
Sample 101	Sample 102
	
Spray drying T-220^{O}C, drying of sample (only drying)	

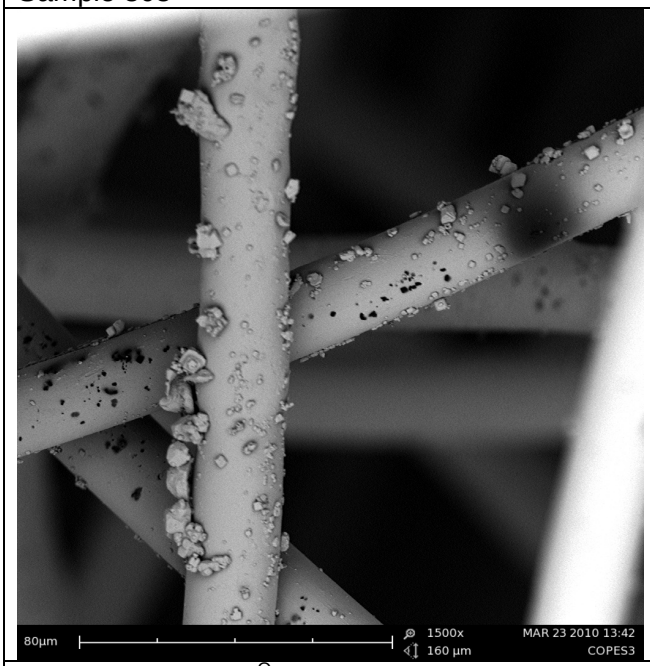
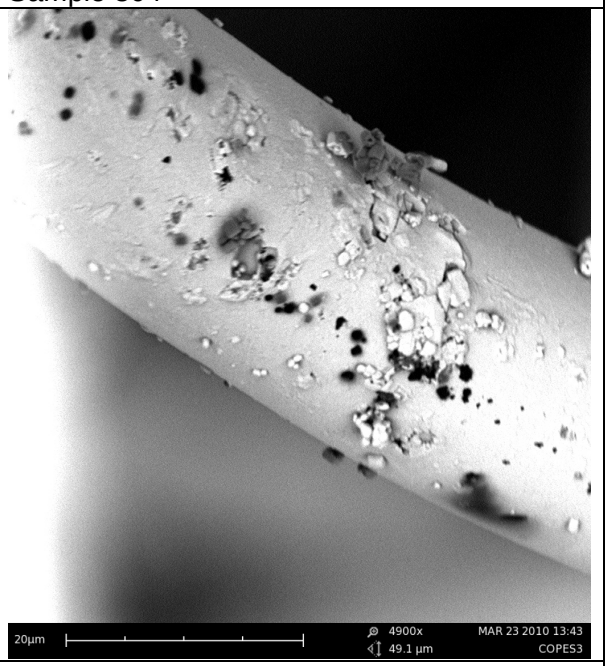
Sample 103	Sample104
	
Spray drying T-220^{O}C, drying of sample (only drying)	

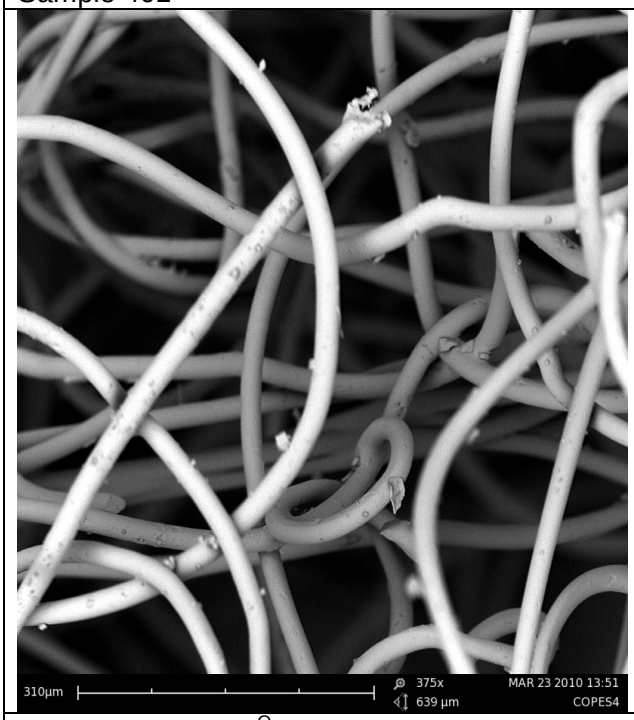
Sample 201	Sample 202
	
Spray drying T-220^{O}C, drying of sample (washing of samples)	

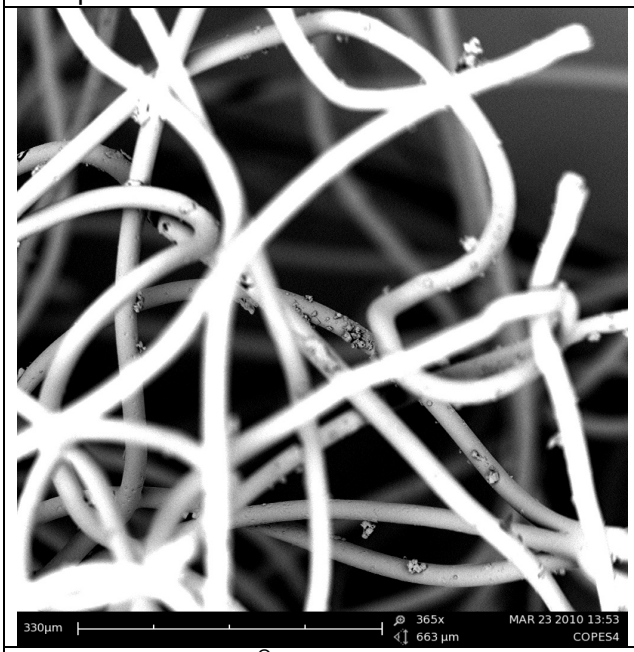
Sample 203	Sample 204
	
Spray drying T-220^{O}C, drying of sample (washing of samples)	

Appendix 6: Second application of sodium chloride directly on bicomponent fibers by drying

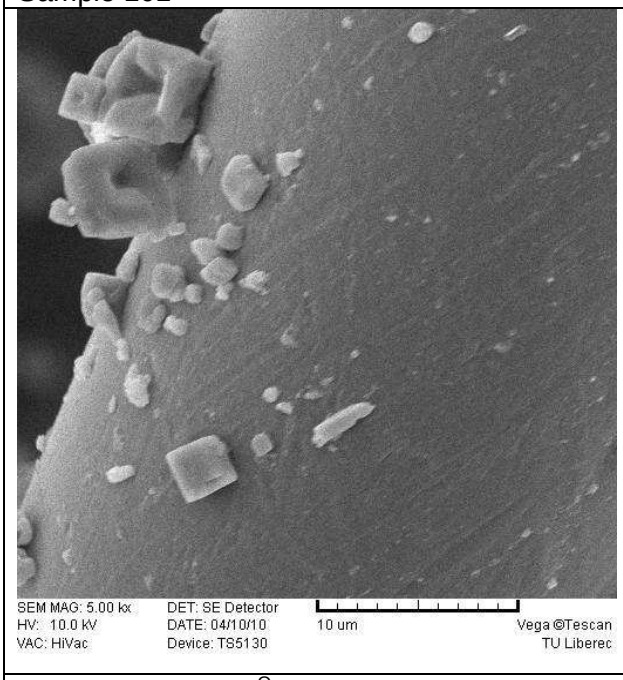
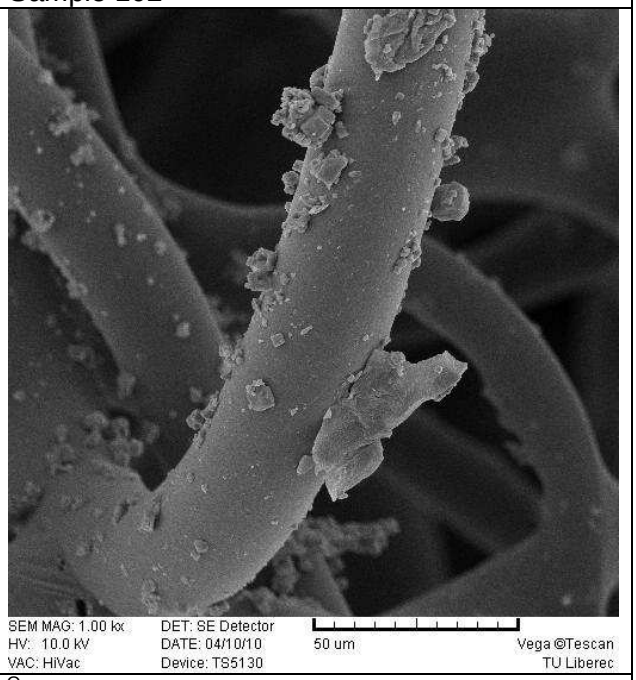
Sample 301	Sample 302
	
Spray drying T-140^{O}C, drying of sample (only drying)	

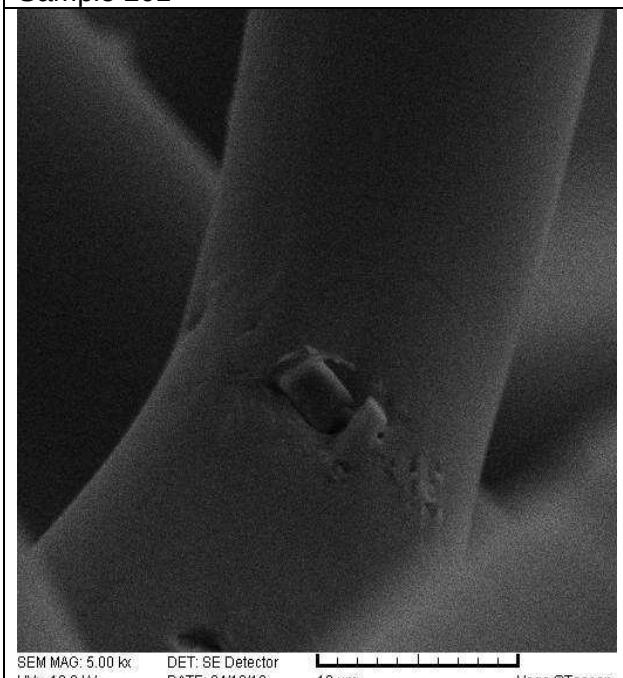
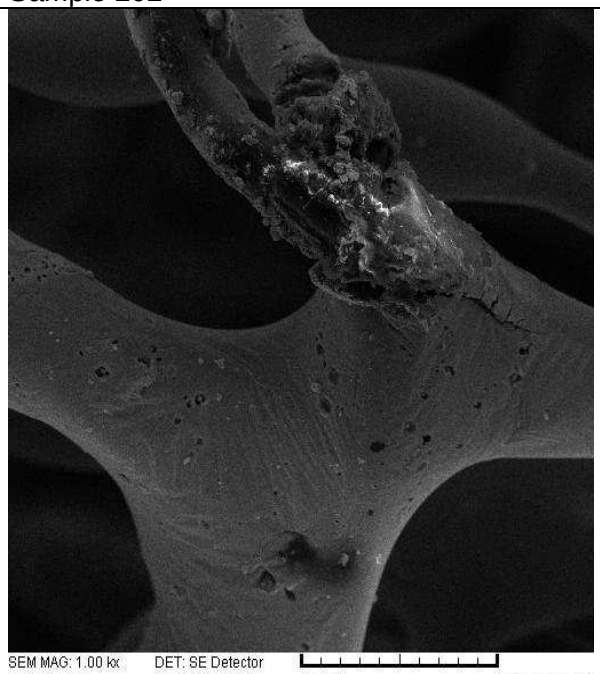
Sample 303	Sample 304
	
Spray drying T-140^{O}C, drying of sample (only drying)	

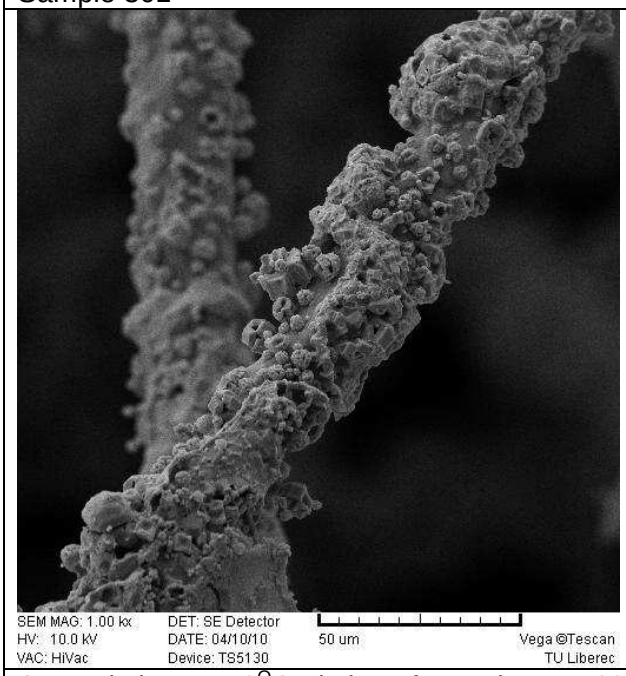
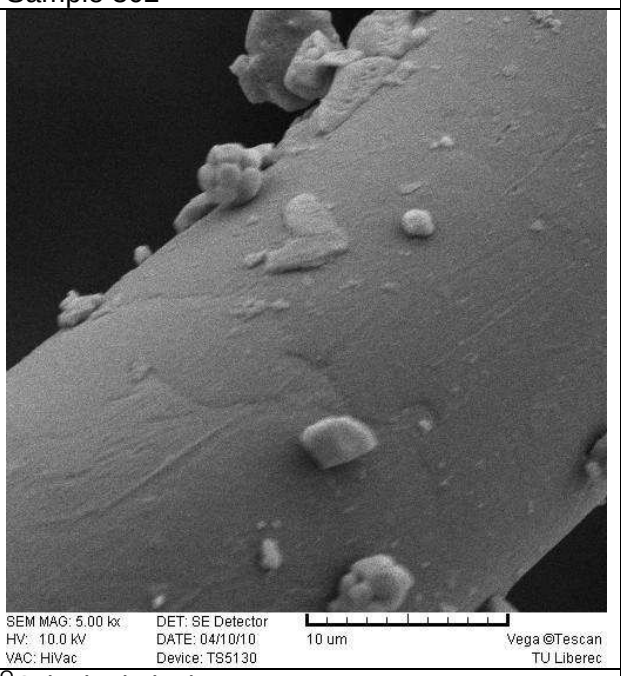
Sample 401	Sample 402
	
Spray drying T-140^{O}C, drying of sample (washing of samples)	

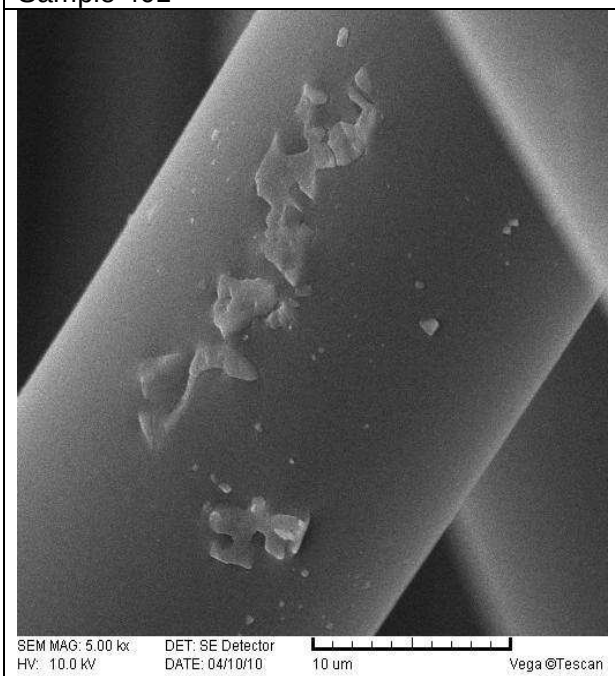
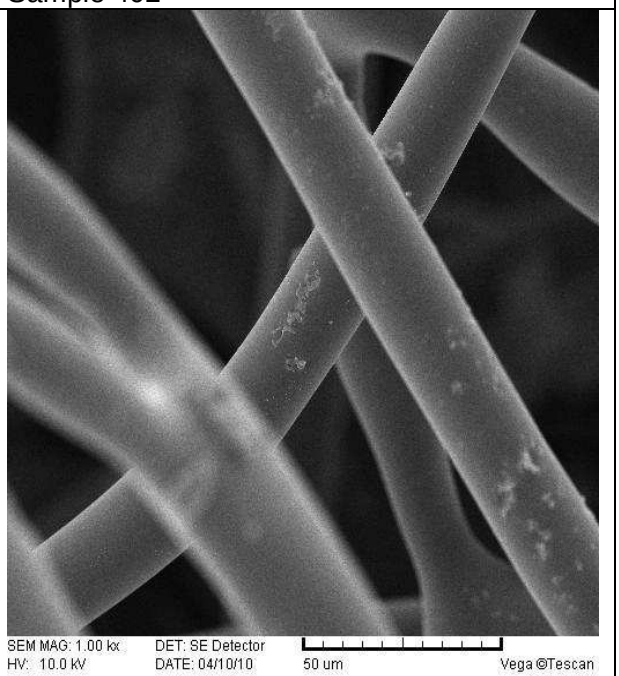
Sample 403	Sample 404
	
Spray drying T-140^{O}C, drying of sample (washing of samples)	

Appendix 7: Drying of treated bicomponent fibers using high temperature

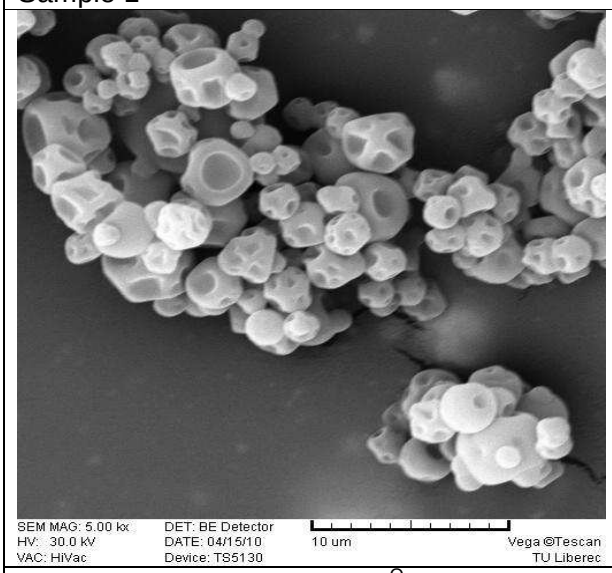
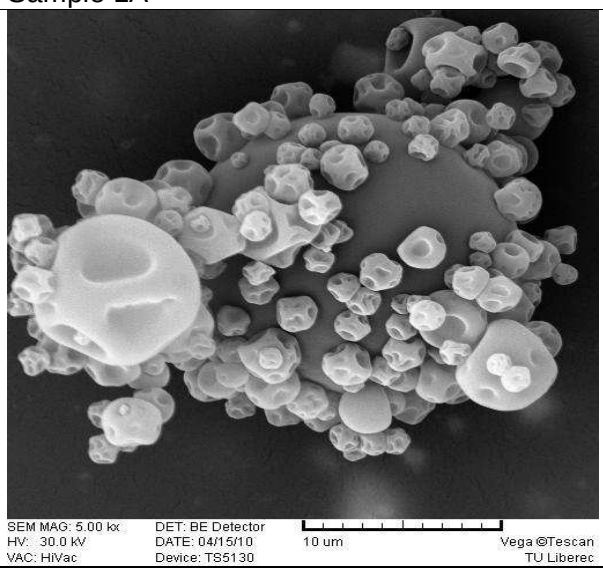
Sample 101	Sample 102
	
Spray drying T-220^{O}C, drying of sample at T=240^{O}C (only drying)	

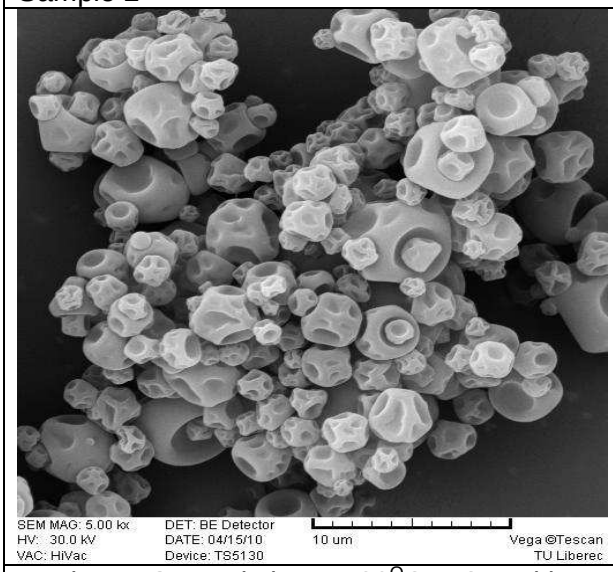
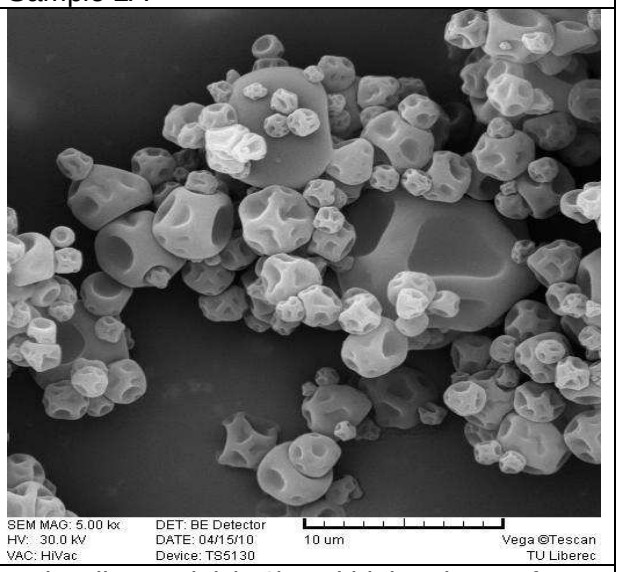
Sample 201	Sample 202
	
Spray drying T-220^{O}C, drying of sample at T=240^{O}C (washing of sample)	

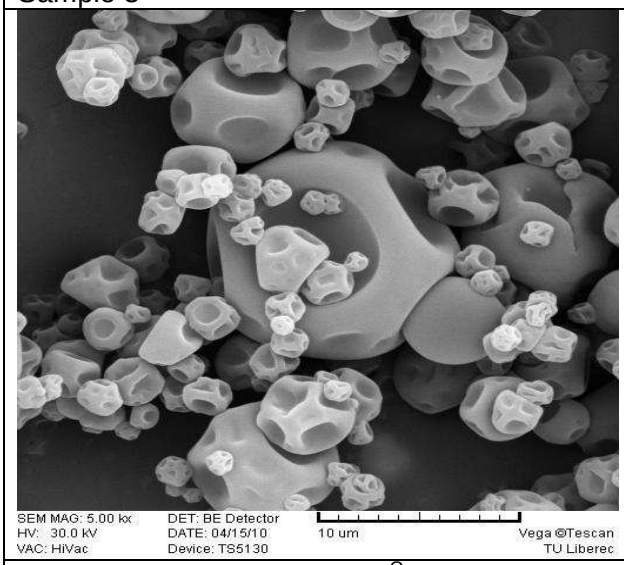
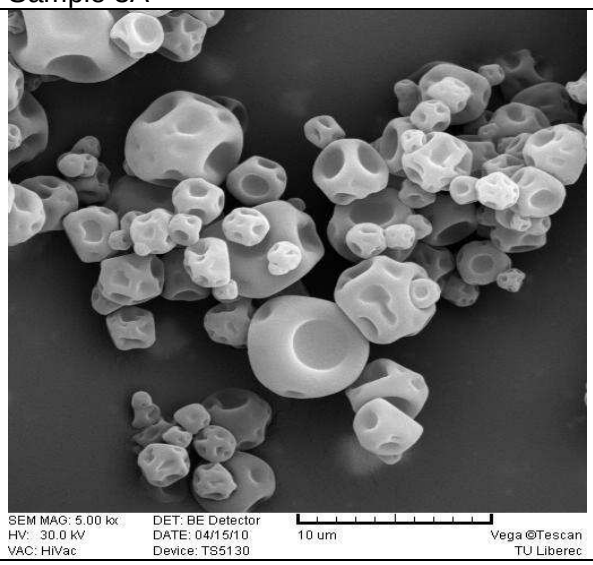
Sample 301	Sample 302
	
Spray drying T-140^{O}C, drying of sample at T=200^{O}C (only drying)	

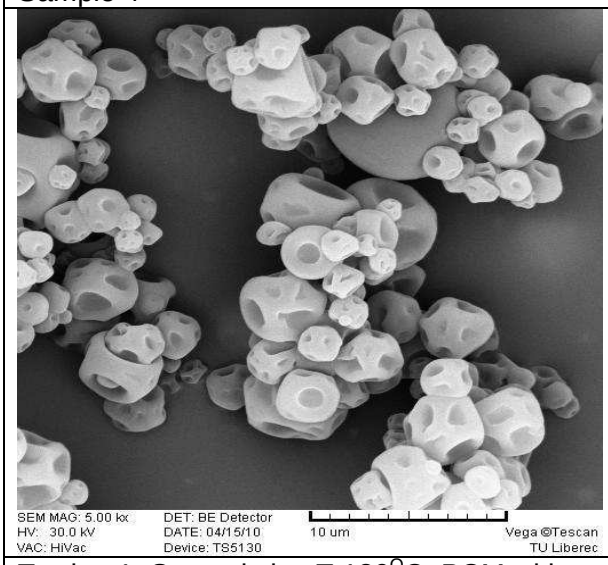
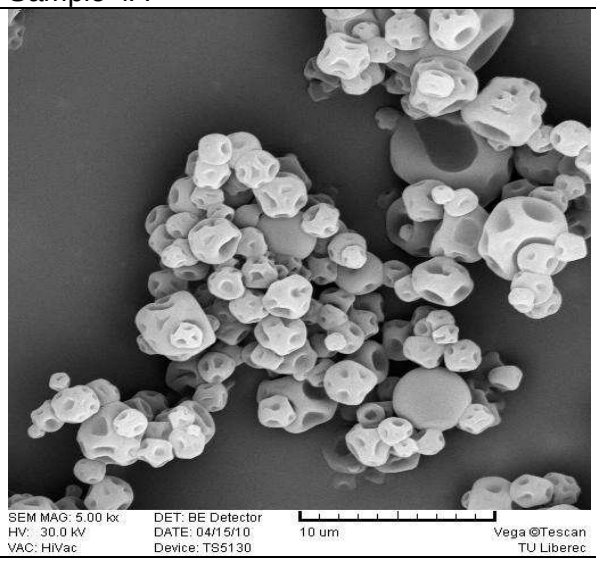
Sample 401	Sample 402
	
Spray drying T-140^{O}C, drying of sample at T=200^{O}C (washing of samples)	

Appendix 8: Encapsulation of phase change material using different ratio of core and wall material

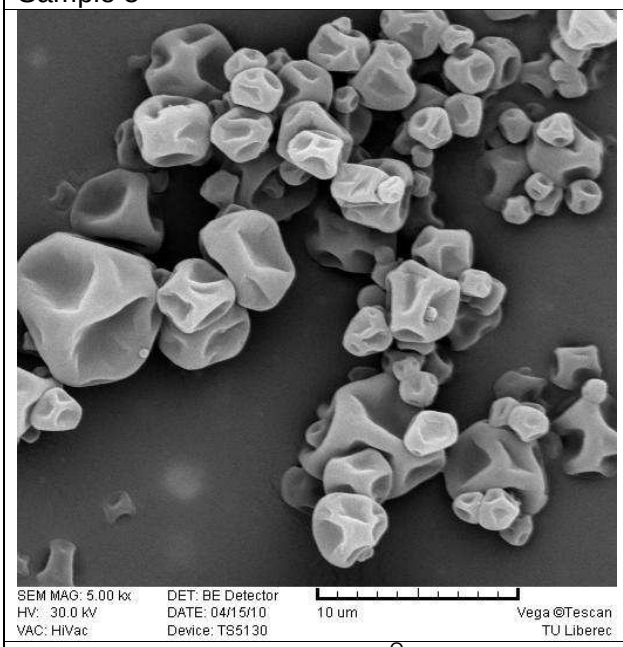
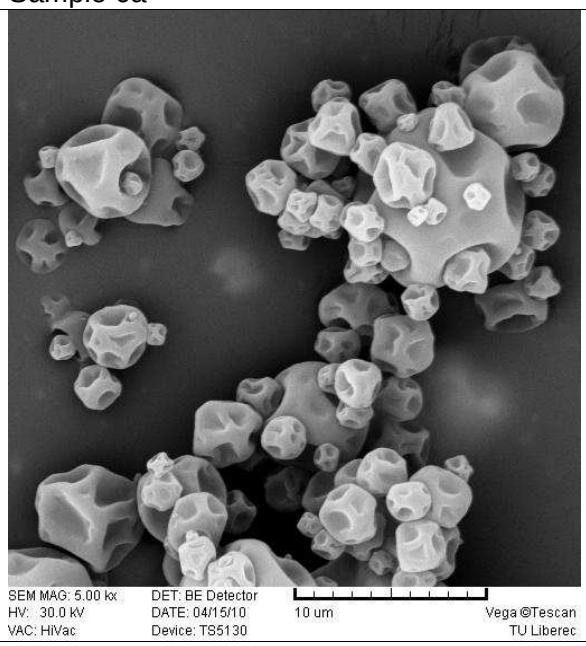
Sample 1	Sample 1A
	
Testing 1=Spray drying T-130^{O}C, PCM with core and wall material (1:1) and small volume of water	

Sample 2	Sample 2A
	
Testing 1=Spray drying T-130^{O}C, PCM with core and wall material (1:2) and high volume of water	

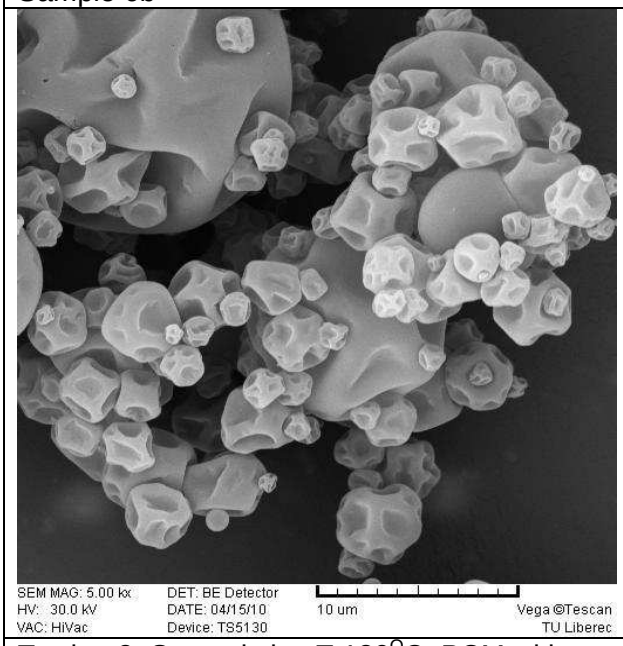
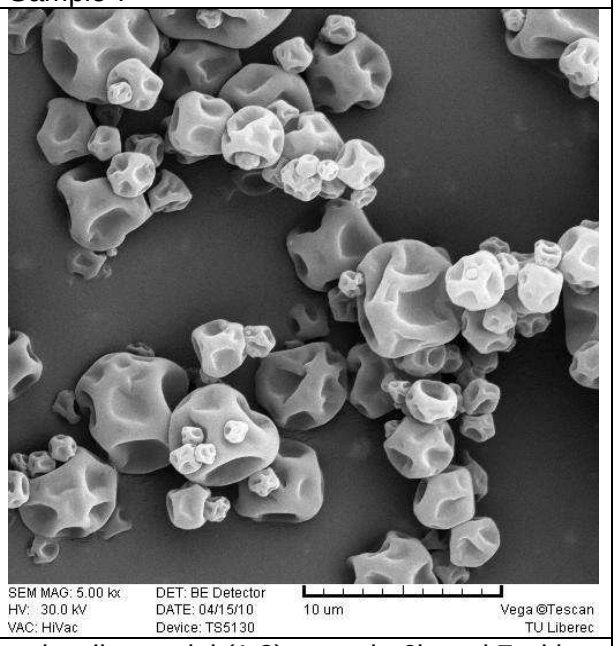
Sample 3	Sample 3A
	
Testing 1=Spray drying T-130^{O}C, PCM with core and wall material (1:1) and high volume of water	

Sample 4	Sample 4A
	
Testing 1=Spray drying T-130^{O}C, PCM with core and wall material (1:2) and small volume of water	

Appendix 9: Encapsulation of phase change material using different melting temperatures of paraffin wax

Sample 5	Sample 6a
	

Testing 2=Spray drying T-130^{O}C, PCM with core and wall material (1:2), sample 5 and 6a with melting temperature ranging [42-44^{O}C] and [50-52^{O}C] respectively

Sample 6b	Sample 7
	

Testing 2=Spray drying T-130^{O}C, PCM with core and wall material (1:2), sample 6b and 7 with melting temperature ranging [50-52^{O}C] and [58-60^{O}C] respectively